STUDIES IN THE SYSTEM

H_2SO_4 — $H_2S_2O_7$

PART I. VAPOUR PRESSURE OF FUMING SULPHURIC ACID

PART II. DIELECTRIC DISPERSION OF SULPHURIC ACID

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C O N T E N T S

INTRODUCTION

The interpretation of the kinetics of a reaction in solution in terms of a chemical mechanism, requires a knowledge of the equilibria in the system, of the physical influences described collectively as "solvation", and of the dielectric properties of the solvent. The recent work on the mechanisms of nitration and sulphonation in sulphuric acid (1, 2, 3) has directed attention to the fact that the solvation phenomena are only understood in a very qualitative sense, and that many of the physical properties of the system have not been accurately measured. The renewed interest in this field has resulted in a qualitative determination of the ionic species existing in solutions in sulphuric acid from Raman spectral (4) and cryoscopic measurements (5)

Part I of the present work is concerned with the measurement of the vapour pressure of fuming sulphuric acid in a range of temperature and composition (0-35% "free" sulphur trioxide) where only fragmentary results are recorded in the literature. These measurements were made partly for their own sake, as information on the equilibria established in the liquid phase, and partly to obtain data required for the

interpretation of the kinetics of sulphonation. The kinetics suggest that the sulphonating agent in oleum is the ion SO_3^+H (3), and it is shown that the concentration of this ion is given by

$$\log [SO_3^+H] = A + \log p_{SO_3} - H_0 - \log \left[\frac{\gamma_{SO_3^+H} \cdot \gamma_B}{\gamma_{HB^+}}\right] \qquad (I)$$

where A is constant at constant temperature, H_0 is the acidity function (6), p_{SO_3} the partial vapour pressure of sulphur trioxide and the γ's are activity coefficients relative to a standard state in sulphuric acid. Consistent values of p_{SO_3} at 25°C were needed to test this hypothesis.

Hammett with Deyrup (7), and with Treffers (8), discovered that electrolyte solutions in sulphuric acid are nearly ideal at concentrations at which, in aqueous solutions, even the Debye-Hückel expression fails and pointed out that interionic forces in sulphuric acid solutions must be unusually small. Gillespie, Hughes and Ingold (5) assume that these forces are completely negligible and draw the conclusion that "interionic activity effects are so weak as to require that the dielectric constant of sulphuric acid shall be very much greater than that of any solvent whose dielectric constant has yet been measured". However, the measurements of the dielectric properties of sulphuric

acid, in Part II, show that this view is mistaken and that sulphuric acid ($\epsilon \sim 110$) is not more extreme, dielectrically, than formamide ($\epsilon \sim 111$ (9)) or liquid hydrogen cyanide ($\epsilon \sim 115$ (10)). The very interesting question of the apparent thermodynamic ideality of solutions in sulphuric acid is briefly discussed in the final section.

PART I.

THE VAPOUR PRESSURE OF FUMING SULPHURIC ACID

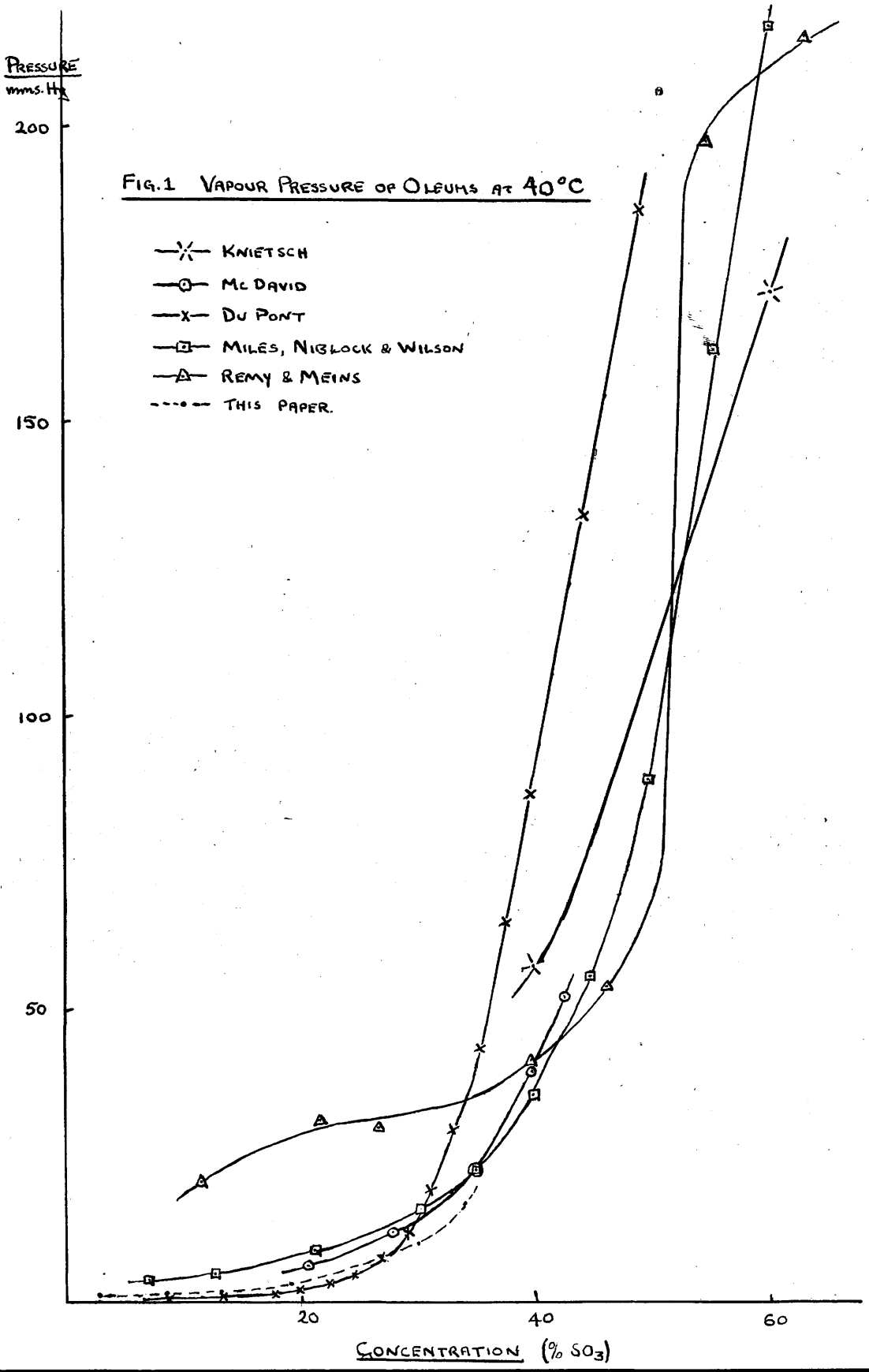


FIG. 1 VAPOUR PRESSURE OF OLEUMS AT 40°C

PREVIOUS DETERMINATIONS

Five series of values for the vapour pressure of oleums are to be found in the literature, and their diversity is obvious from Fig. 1.

The earliest determination is that of Knietsch (11) who examined oleums in the concentration range 30–100% "free" sulphur trioxide at temperatures between 35° and 100°C. Concerning the experimental method, Knietsch is vague, stating "on this account (that mercury is attacked by sulphur trioxide) the measurements were carried out in an iron apparatus fitted with a manometer which was sufficiently accurate for the purposes of the experiment". The vapour pressures are tabulated for 10% intervals in sulphur trioxide concentration and may possibly be a set of smoothed values and not the experimental results. This table was headed "3/4 oleum and 1/4 air", from which one may infer that the vessel was three-quarters full with acid and the remainder with air at atmospheric temperature and pressure, the latter being allowed for in the subsequently measured pressures. The fact that air was left in the apparatus introduces an unknown factor, namely the change of solubility of air in oleum with change in temperature; Knietsch makes no mention of this.

The reactivity of sulphur trioxide makes measurements of its pressure troublesome, and the method devised by McDavid (12) was designed to eliminate direct pressure measurement. The results relate to oleums with vapour pressures in the range 5 to 50 mms. Hg. at temperatures between 40° and 90°C, and the concentrations were in the range 2-43% "free" sulphur trioxide. The method was to pass a constant stream of mixed gases (SO_3, O_2, and a trace of SO_2) from the catalytic oxidation of sulphur dioxide into sulphuric acid or oleum at a known temperature (within ± 1°C) until the resulting oleum was of constant composition. McDavid assumed the vapour pressure of these oleums to be equal to the partial pressure of the sulphur trioxide in the gas stream, and calculated the latter from the known conversion (98%) and the pressure and composition of the initial sulphur dioxide-oxygen mixture. There is no objection to the assumptions, and the accuracy of this method should be limited by the large temperature tolerance.

An otherwise unpublished set of results was contributed to "International Critical Tables" by the Eastern Laboratory of Messrs. du Pont (13). The results fall in the range 8.89% to 66.7% "free" sulphur trioxide

between 20°and 90°C with pressure not in excess of 500 mms. Hg. No experimental details are available, and since the data are given for intervals of 0.5% H_2SO_4 and fit very closely to linear log p vs. 1/T plots it would appear that these are smoothed values.

More recently two further determinations have been made. Miles, Niblock and Wilson (14) have measured the vapour pressure of six oleums whose concentrations lie in the range 6.89% to 64.7% "free" sulphur trioxide, the measurements being limited to a maximum temperature of 170°C or a pressure of 950 mms. Hg. The measurements were carried out in an all-glass system using a glass Bourdon gauge. Considerable care was exercised to remove all extraneous gases and vapours from the oleums; and the method should have produced results of high accuracy. However, the manner in which the gauge was used can be criticised. An arbitary reference point was used, such that the pressure required to bring the pointer to this position was always in excess of the pressure measured, and the true pressure was obtained by subtracting the pressure required to bring the gauge to this position when one side was evacuated. It will be shown later that this method is liable to error which is more serious at low than at high pressures. For the weaker oleums, the

vapour pressures at the lower temperatures deviated, in the sense of excess pressure, from the linear log p vs. 1/T graphs on which the values at higher temperatures lay. Miles attempted no explanation of this, beyond remarking that it did not seem to be due to experimental error; he ultimately neglected all pressures below 12 mms. Hg.

Finally, Remy and Meins (15) have measured the vapour pressure of oleums containing 11.1% to 97.5% "free" sulphur trioxide between 20° and 40°C. These authors also used the static method, measurements being carried out in an all-glass apparatus with a Bodenstein spiral quartz gauge as a null instrument. The oleums were not degassed; instead a known pressure of air (~10 mms.) was left in the apparatus and allowed for in the subsequent measurements. Thus these results are open to the same criticism as Knietsch's since the variation with temperature of the solubility of air in oleum is not taken into account. This criticism is supported by the fact that these authors did not really attain equilibrium at each temperature, since they invariably obtained a higher vapour pressure when the equilibrium was approached from a higher temperature than when it was approached from below.

METHODS AND SCOPE OF PRESENT INVESTIGATIONS

Methods of Measurement of Vapour Pressures.

Vapour pressures may be determined by three principal methods.

(i) The dynamic method, in which the temperature at which a liquid boils under a known pressure, or the pressure at which a liquid boils at known temperature is determined. The vapour pressure is considered to be equal to the applied pressure. This method is subject to error due to super-heating, and has generally been superseded by the two following methods.

(ii) The transpiration method, in which a stream of inert gas is saturated with the vapour and the uptake of vapour determined, requires that the removal of the vapour does not disturb the liquid-vapour equilibrium. This condition is satisfied if the flow of inert gas is slow compared to the rate of transfer of a molecule from the liquid to the vapour phase. For accurate work with solutions, the change in concentration caused by the removal of vapour must be negligible.

(iii) The static method, in which a sample of the liquid is freed from all gases and sealed in a vessel to which a manometer is attached. The apparatus is allowed to come to thermal equilibrium at the desired

temperature and the vapour pressure is read from the manometer.

In the system sulphur trioxide-sulphuric acid, it is generally accepted that the equilibrium between the components lies well to the right of equation (II).

$$H_2SO_4 + SO_3 \rightleftharpoons H_2S_2O_7 \qquad (II)$$

Evidence is afforded for this from the existing vapour pressure data where the pressure is seen to increase only slightly with increase in sulphur trioxide concentration until the system approaches the composition corresponding to disulphuric acid ($H_2S_2O_7$) when a very rapid increase in pressure occurs. Further support is provided by Millen's interpretation (4) of the Raman spectra of oleums. He showed that addition of sulphur trioxide to sulphuric acid brought about a decrease in the intensity of the frequencies attributed to sulphuric acid, together with the appearance of new frequencies of increasing intensity ($H_2S_2O_7$). The frequencies attributed to sulphur trioxide and higher polysulphuric acids ($H_2S_3O_{10}$, $H_2S_2O_{13}$) do not appear until the composition approximates to disulphuric acid.

To maintain the equilibrium, the transfer of sulphur trioxide from the liquid to the vapour phase must be followed by dissociation, according to equilibrium (II),

of disulphuric acid. If either the dissociation or the transference from the liquid is slow then the determination of vapour pressure by the transpiration method does not yield correct values, unless it can be ensured that the rate of removal of vapour is less than the rate of the process supplying it. Accordingly, the static method, employing a manometer resistant to sulphur trioxide was considered preferable .

Manometers for Corrosive Gases and Vapours.

Various manometers have been developed for use with reactive gases or vapours, but for pressures of the order of 0.1 mm. Hg. and upwards, they all depend upon the principle of physical deformation by pressure differences. These are of three types:-

(i) The gauge developed by Bodenstein (16) is in the form of a spiral of thin tubing. Silica is prefered to glass because of its higher elasticity.

(ii) The "Bourdon" type gauge, introduced by Jackson (17), is made by collapsing one side of a thin bulb of either glass or silica; glass is usually used for convenience in fabrication. This gauge is also refered to as the "Spoon" or "Sickle" gauge.

(iii) The "Diaphragm" gauge, whose principle is that of the aneroid barometer, consists of a thin flat

membrane of glass or silica sealed to the end of a tube; mica and metal diaphragms waxed or cemented in place have been used in some instances.

The first two types are generally preferred since they are less fragile, and are normally operated as null instruments by balancing the unknown pressure with air and measuring the air pressure on a mercury manometer.

A glass Bourdon gauge was adopted for the present investigation. To obtain high sensitivities directly with these gauges it is necessary to employ very thin bulbs which withstand pressure differences of only a few mms. Hg. Some form of mechanical magnification of the movements is often resorted to in order that a robust gauge may have a high sensitivity. Lewis and Style (18) obtained sensitivities of the order of 10^{-4} mm. Hg. by the use of a magnetically damped bifilar suspension attached to the pointer, but the zero position is only reproducible for short periods; this is a serious objection for the present purpose in which the zero position must remain constant for several days. By using a system of glass levers connected by filaments of glass, Foord (19) obtained sensitivities of 0.1 mm. Hg. but this system is fragile and is best operated with the lever system suspended below the bulb. Barnartt and

Ferguson (20) employed a short, freely suspended lever deflected by the pointer, the movement of the lever being observed by a conventional optical system, and obtained sensitivities of 0.02 mms. Hg. The system was susceptible to vibration and needed a special mounting. Using the same principle, but by constructing a very much lighter lever than Barnartt and Ferguson, it has been possible to obtain sensitivities of 0.02 mms. Hg. without the system being unduly sensitive to vibration. These gauges were calibrated as direct reading instruments at low pressure. At higher pressures, a pressure of air (slightly less than that being measured) was admitted to the outside of the gauge and the unknown pressure observed as the sum of the external pressure of air and the pressure deduced from the residual deflection, the external pressure being read on a conventional mercury manometer.

The technique adopted was similar to that of Miles (14). The measurements were carried out in a glass apparatus in which the number of stopcocks was reduced to a minimum (since the grease is attacked by sulphur trioxide). Breakable glass seals were employed instead of stopcocks, where necessary, and the used parts

of the apparatus were sealed off when finished with. It was found convenient to obtain the pressure-temperature relation for different oleums, each oleum being freshly prepared *in situ* by distilling degassed sulphur trioxide into degassed sulphuric acid and analysed after the measurements. Temperatures between 10° and 80°C were controlled to within 0.1° by immersing the liquid under test and the Bourdon gauge in a thermostated water-bath.

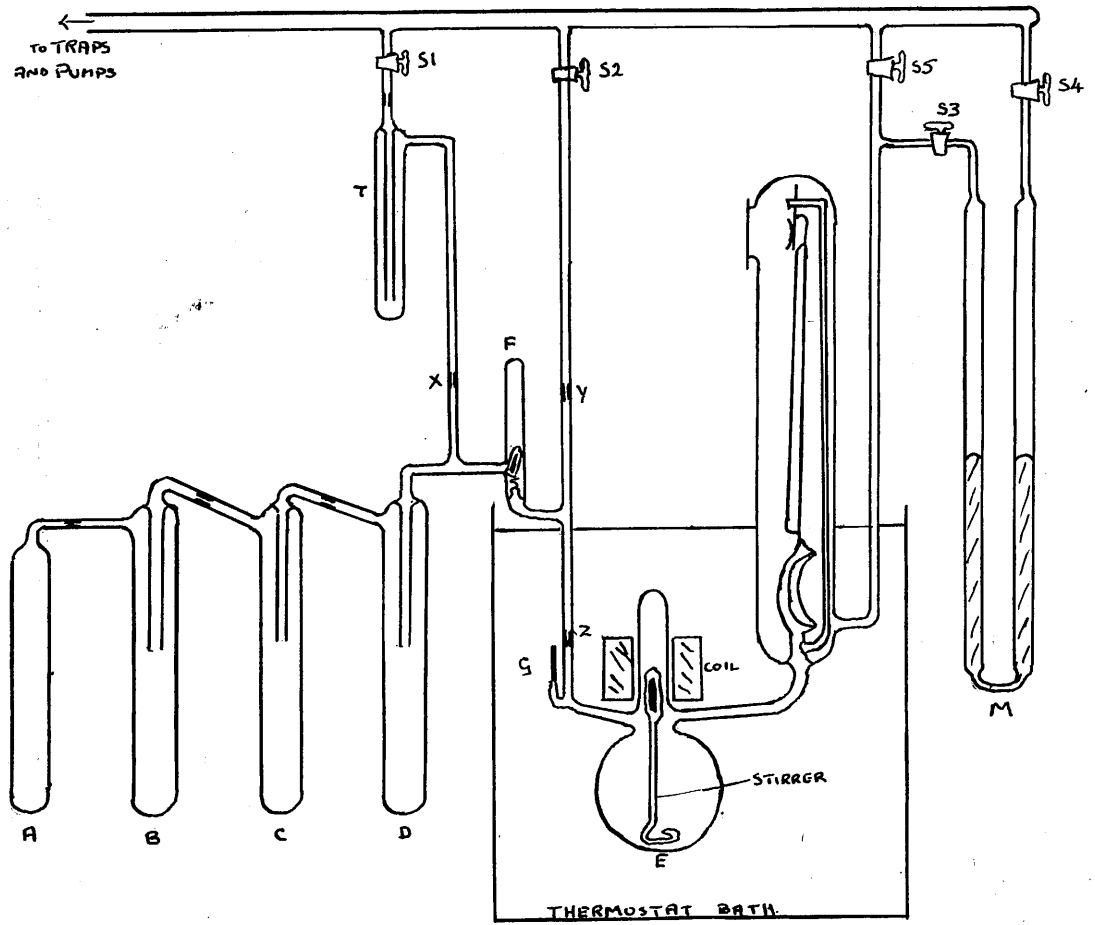


FIG. 2. DIAGRAM OF APPARATUS

EXPERIMENTAL

Apparatus

The complete apparatus, shown diagrammatically in Fig. 2., was constructed from Pyrex glass, and could be evacuated to less than 10^{-5} mm. Hg. by a two stage mercury diffusion pump backed by a rotary oil pump. All stopcocks and ground joints were lubricated with Apiezon "M" grease. The stirrer, constructed from glass with an iron core sealed in the top, was operated electromagnetically. The function of the various parts will be clear from the details of the technique.

Adaption of Bourdon Gauges for Increased Sensitivity

Initial experiments with systems of glass levers interconnected with glass fibres showed that the latter were too brittle if they were not to offer too great a resistance to movement.

The requirements of a sensitivity of at least 0.1 mm. Hg., relative insensibility to vibration, and capable of upright mounting (necessitated by the thermostat), were met using the system shown in Fig. 3. The tip of the pointer A was forked and against it at B bore a short length of fine thin walled glass tubing, which was suspended from a rigid support C by a fine copper wire (ca 40 S.W.G.). The wire was sealed directly

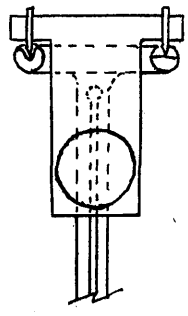
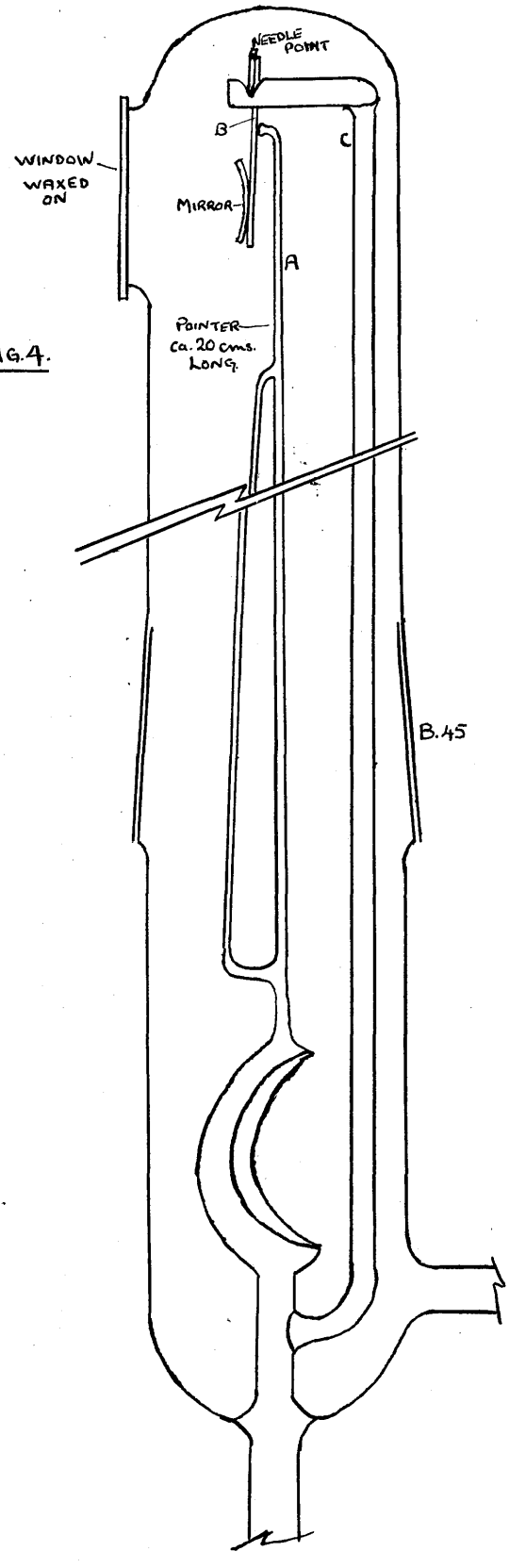


FIG.4.



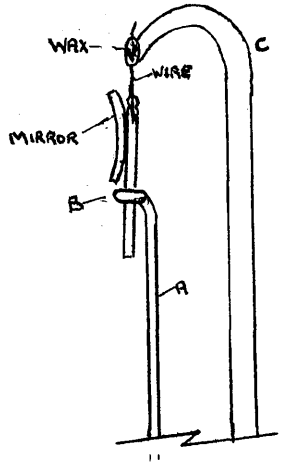


FIG.3

DETAILS OF GAUGE ASSEMBLIES

into the thin tube and attached to the support by hard vacuum wax (Apiezon "W"). The angular motion of this short lever was observed by a conventional optical system, a light galvanometer mirror being attached with wax, and the movement of the image being observed on a millimetre scale 1.35 metres distant. Deflections of up to 6 scale divisions per mm. Hg. difference in pressure were obtained, and since the position of the image could be estimated to 1/4 of a scale division this represented sensitivities of up to 0.05 mm. Hg. and magnifications of ca. 10. The copper wire was sufficiently flexible to allow deflections of over 200 scale divisions without a permanent bend being imparted. No special damping of vibrations was employed, ordinary clamps being used to hold the gauge casing to the framework.

The need for higher sensitivities was met by the assembly shown in Fig. 4. The lever took the form of a sheet of thin copper B (ca. 26 S.W.G.) to which was soldered two needle points. The support for this consisted of a U-shaped piece of glass tubing sealed to a rigid support C, and containing a pit and a slot in the arms to act as bearings for the needle points. The pit and the slot were made by pressing a needle point and the edge of a razor blade, respectively, into the softened

glass. The pointer A attached to the bulb was built up from 1 mm. glass rod as this gave a greater rigidity for a given weight compared to the single rod pointer. The motion of the lever was observed by the same optical system described above. Deflections of up to 38 scale divisions per mm. Hg. pressure difference were obtained, but the position of the image could only be estimated to 1/2 to 1/3 of a scale division, equivalent to a maximum sensitivity of 0.01 mm. Hg. This seems to represent the limit attainable with this assembly without taking special precautions to reduce the effect of vibration. It was necessary to switch off all pumps and motors attached to the apparatus whilst a reading was actually being taken. Provided that the sides of the bearings were made steep, considerable deflections, over 300 scale divisions, were possible before the assembly began to lift from its bearings.

Measurement of Pressure with Bourdon Gauge

For small pressures, and for pressure differences, the gauges were operated as deflection instruments. Small pressures were interpreted directly from the deflection with the outside evacuated, and larger pressures were partially compensated by admitting a pressure of air (slightly less than the

unknown pressure) to the outside of the gauge, the total pressure being observed as the sum of the compensating pressure and the excess pressure interpreted from the residual deflection. This method, which avoided the exact balancing of pressure required when the gauges are used as null-point instruments, has been used successfully with Bodenstein "spiral" gauges (21).

Calibration of the gauges, to obtain the pressure-deflection relation, was carried out after they had been built into the apparatus shown in Fig. 2. The apparatus was evacuated to less than 10^{-4} mm. Hg., the two sides of the gauge isolated by closing stopcock S5 and dry air admitted to E. The pressure of the air was measured on the wide bore (12 mms.) mercury manometer, M, with a cathetometer, and the deflection of the gauge noted. The calibrations were carried out at several temperatures for each gauge. For the low sensitivity assembly (Fig. 3.) the pressure-deflection relation was found to be linear for deflections up to 250 scale divisions (the limit of measurement), but at the higher sensitivities (Fig. 4.) slight deviations from linearity were observed in some instances. In all cases the calibration was independent of temperature over the range 10°to 80°C, and did not change with age, but this does not exclude the

possibility of an initial "settling down" since no bulb was used immediately it was blown.

In some cases the null point of the gauge was subject to a small, but reproducible, variation with temperature and the correction applied for this was obtained by cycling the thermostat bath over the working temperature range with the gauge evacuated.

A possible source of discrepancy with the results of other workers was examined as follows. A gauge, sensitive to 0.05 mm. Hg., was used in the manner of Miles (14) by taking an arbitrary reference point so that the pressure required to bring the pointer to this position was always greater than the pressure within the gauge. The results are shown in Table 1. Miles assumed that the true pressure was obtained by subtracting the pressure needed to bring the pointer to the arbitrary reference point when one side (inside) was evacuated, from that required to bring the pointer to the same position when an unknown pressure existed inside the gauge. If this assumption is correct, the first and fourth columns in Table 1 should be identical. The pressures deduced by this method are found, however, to exceed the real values (column 5, Table 1), the percentage error decreasing with increase in pressure.

Table 1. Accuracy of Gauge Handling.

1. True Pressure	2. Pressure to bring to natural zero	3. Pressure to bring to arbitrary zero	4. Pressure deduced from arbitrary zero	5. Δ (4–1)
0.00	0.00	4.15	–	–
5.00	4.95	9.60	5.45	0.45
14.30	14.30	19.00	14.85	0.55
20.75	20.70	25.35	21.20	0.45
44.30	44.30	49.00	44.85	0.55
74.70	74.70	79.45	75.30	0.60

The agreement between the first and second columns justifies the normal use of the gauge as a null instrument.

Preparation of Oleums

A stock of strong oleum (ca.65% "free" SO_3) was prepared by distilling the sulphur trioxide from a commercial oleum, which had been treated for 24 hours with chromium trioxide to remove sulphur dioxide (22), into concentrated "Analar" sulphuric acid in an all glass apparatus.

A known amount of this oleum was placed in A (Fig. 2), which was sealed onto the apparatus. The contents of A were cooled to -78°C (CO_2-EtOH), and the apparatus evacuated to ca. 10^{-3} mm. Hg. During this, and all subsequent evacuations, all accessible parts of the apparatus were heated to remove adsorbed gases, particular attention being paid to the constrictions provided for sealing off. Stopcock S1 was closed, trap T cooled in liquid oxygen (to protect S1 from attack by sulphur trioxide), trap B cooled to -78°C, and the sulphur trioxide only was allowed to distill from A by warming the latter to ca. 40°C. At the finish of the distillation, stopcock S1 was opened, A sealed off, and evacuation continued to reduce the pressure of residual

gas to less than 10^{-4} mm. Hg.* Stopcock S1 was closed and the sulphur trioxide distilled into C, by cooling the latter to -78°C and warming B slightly if necessary; B was then sealed off while the section was further evacuated. This procedure was repeated to transfer the sulphur trioxide into D. After further evacuation, D was sealed off from the pumps at X, and trap T was also removed. Thus a sample of sulphur trioxide, rendered free from all gases by repeated distillations and by evacuation for a total period of 6 to 7 hours at less than 10^{-4} mm. Hg., was obtained completely enclosed in glass.

A known amount of "Analar" concentrated sulphuric acid, placed in E prior to assembling the apparatus, was degassed meanwhile by heating to ca. 90°C in a water-bath, with occasional stirring while the residual pressure was maintained at less than 10^{-4} mm. Hg., for 5 to 7 hours. E was sealed off from the pumps at Y.

The above pressures were estimated from the high frequency discharge in the system, since, because of the constrictions, a McLeod gauge reading would be meaningless unless directly attached above the trap in which it was desired to measure the pressure. Furthermore, it was considered advisable to eliminate mercury vapour from the system completely during these

* Vapour pressure of SO_2 at -80°C is 8 mms. Hg. (23).

stages, and stopcocks S3 and S4 were kept shut.

Flask E and trap D were connected by breaking the seal F, and the sulphur trioxide allowed to distill into E which was cooled in ice-water. When the distillation was complete, trap D was cooled in liquid oxygen, E cooled to -78°C and the latter sealed off at Z. The reading of the gauge was checked at this stage, and, within the experimental error, was found to coincide with the "zero" position. E was then allowed to warm up to room temperature, it being expedient to hasten the melting of the top of the solid in contact with the flask by warming with the fingers. This latter precaution eliminated fracturing of the flask by the expansion of the contents which Miles (14) found troublesome, being aggravated in their case because the sulphur trioxide was distilled onto sulphuric acid cooled to -78°C, and a rapid expansion occured on warming, due to the heat of solution, whilst the top of sulphur trioxide layer was still solid.

By adjusting the initial amounts of stock oleum and sulphuric acid, a colourless oleum approximating to any desired strength and free from sulphur dioxide could be obtained.

Measurement of Vapour Pressure of Oleums

The apparatus was surrounded (Fig. 2) by a well-

stirred water-filled thermostat which could be adjusted and maintained to 0.05°C at the lower temperatures and 0.10°C at the upper temperatures. The temperatures were measured by two mercury-in-glass thermometers, one 0 -50°C graduated in 1/5 ths., and the other 50 -100°C in 1/10 ths. Above 50°C, evaporation was retarded by covering the water surface with a layer of paraffin wax (m.p. 45°C), which solidfied and was removed when the tank cooled.

Measurements were taken by adjusting the bath to the required temperature, and allowing the oleum and its vapour to come to thermal equilibrium as indicated by a constant value of the vapour pressure for a period of at least an hour. The oleums were frequently stirred during the measurements, but (cfr. Miles (14)) it was found that this was not essential, only serving to reduce the time required to reach thermal equilibrium. The greater surface/volume ratio afforded by the spherical vessel, compared to the cylindrical vessel used by Miles, probably accounts for stirring being less important. Equilibrium was normally approached from below, but at two or three temperatures it was also approached from above to ensure that equilibrium had been attained. This procedure was applied at each concentration, and the same pressure was invariably observed, within experimental error,

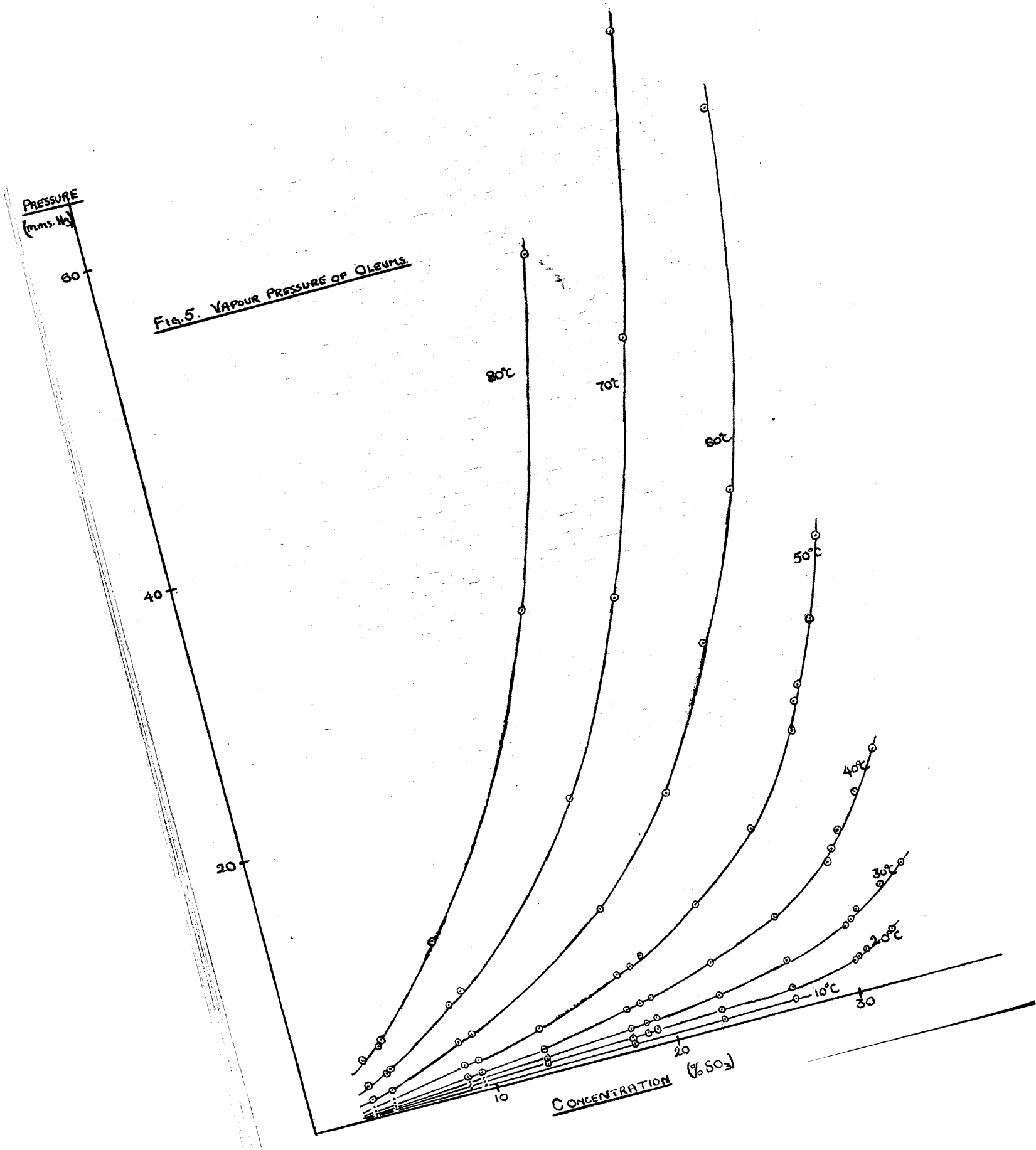


FIG. 5. VAPOUR PRESSURE OF OLEUMS.

irrespective of the direction from which equilibrium was approached.

Analysis of Oleums

To safeguard the gauge, the following technique was adopted for opening the flask E. The side arm G terminated in a thick-walled capillary (ca. 1 mm. O.D.). The capillary was scratched with a file, one end of a length of thin pressure tubing was pushed over it and the other end of the tubing over the arm of stopcock S1, and then roughly evacuated. The capillary was broken inside the tubing and dry air slowly admitted to the apparatus. In this manner the gauge was not submitted to large differences in pressure.

The oleum was quickly transfered to weighed flasks and its composition determined by titration with water (24) from a microburette. Conditions were controlled so that sufficient oleum was prepared in E to enable at least two titrations of more than 0.5 cc. to be made.

Results

The experimental results are set out in Table 2, and shown graphically in Fig. 5. By the method described it was impossible to duplicate the preparation of an oleum of a particular concentration, but oleums with only

Table 2. Vapour Pressure of Oleums

(in mms. Hg.)

Temp	Concentration (% "free" SO_3)															
°C	3.37	4.50	4.65	8.69	9.37	13.0	17.8	18.6	19.2	22.8	26.7	30.2	30.6	30.9	32.5	34.0
10	0.11	0.12	0.13	0.21	0.25	-	0.43	-	-	0.49	0.62	S	S	S	S	S
20	0.19	0.19	0.20	0.37	0.44	0.55	0.81	0.88	0.97	1.19	1.47	2.18	2.40	2.80	3.70	S
25	-	-	-	-	-	0.75	-	1.17	1.30	-	-	-	-	4.05	5.15	5.40
30	0.33	0.35	0.35	0.63	0.70	0.98	1.48	1.62	1.79	2.27	3.43	4.62	5.10	5.85	7.25	7.95
35	-	-	-	-	-	1.31	-	2.23	2.44	-	-	-	-	8.10	10.10	-
40	0.52	0.52	0.54	1.10	1.25	1.77	2.85	3.03	3.35	4.63	6.65	9.34	10.90	11.50	13.90	16.35
45	-	-	-	-	-	2.43	-	4.21	4.63	-	-	-	-	16.00	19.30	-
50	0.80	0.88	0.95	2.01	2.17	3.22	5.50	5.88	6.37	8.95	13.10	18.95	21.30	22.20	26.60	32.05
60	1.33	1.56	1.68	3.65	4.08	-	10.37	-	-	17.10	26.70	36.85	40.40	-	-	60.25
70	2.25	2.75	2.98	6.40	7.26	-	18.48	-	-	31.45	49.20	67.25	73.10	-	-	109.60
80	3.82	4.84	5.26	11.19	-	-	32.28	-	-	56.65	-	-	-	-	-	-
Gauge No.	10	10	10	11	10	10	11	9	9	12	12	12	12	8	8	12
Sensitivity	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.05	0.05	0.02

S—Oleums Solid.

small differences in composition could be obtained and these provided a check on the reproducibility of the results. Since these determinations were made with different gauges, the number of the gauge and its sensitivity have been included in the table.

Vapour Pressure of Water

A check of the apparatus was made by determining the vapour pressure of water, for which values are accurately known.

The apparatus used was as in Fig. 2, except that the sulphur trioxide traps were removed. Pure distilled water was placed in E, and rendered gas-free by repeating the cycle:- freezing, evacuation to 10^{-4} mm. Hg. and melting; five times. After the fifth evacuation E was sealed off at Z and the measurements performed as described above. The following values (Table 3) were obtained using a gauge sensitive to 0.1 mm. Hg.

Table 3. Vapour Pressure of Water

Temp	15.0	20.0	25.0	30.0	36.0°C
V.P. found.	12.8	17.6	23.7	31.9	44.6 mms. Hg.
V.P. true.	12.79	17.54	23.75	31.82	44.56 mms. Hg.

The true values for the vapour pressure of water were taken from Landolt Bornstein's Tables.

DISCUSSION

Vapour Pressure of Oleums

The values obtained in the present investigation agree exactly with none of the earlier results (Fig. 1.). The values of Knietsch (11) and of Remy and Meins (15) are much in excess of all other data in the region of composition (3-34% "free" sulphur trioxide) under investigation. Both these determinations are open to the objection that the sulphur trioxide was mixed with air during the measurement (p. 7), and the fact that the latter authors did not obtain reproducible results on cycling the temperature, throws further suspicion onto their values. Reasonable agreement with the results of Miles (14) was expected, but the present results are all appreciably lower, although there exists a tendency for the two sets to converge at the higher concentrations. It has been shown that the latter author's results may be high, due to an error introduced in handling the gauge but it seems unlikely that the differences, in some cases of several mms. Hg., are wholly attributable to this cause. The only other essential difference in the method described here and that of Miles was in the preparation of the oleums. In the present preparation the sulphur trioxide vapour was absorbed directly in liquid sulphuric

acid, whilst Miles condensed the sulphur trioxide vapour on sulphuric acid at -78°C and solution occured upon warming.

The data of McDavid (12) do not lie on well defined isothermals, particularly at the higher temperatures, the scatter probably being due to the wide temperature tolerance (±1°C). However, except at 40°C where the results are consistantly higher, the agreement with the present data is better than any other. The values of du Pont (13) lie on isothermals which twice cross the present curves, in the sense that the du Pont pressures are greater in the lower and upper regions of concentration and smaller in the intermediate range. Lack of information concerning these measurements, however, precludes any further discussion of their validity.

The absense of other thermodynamic data for the system prevents any independent check on the vapour pressure results. Miles (14) interpolated his data to obtain boiling points under atmospheric pressure and compared these, not unfavourably, with those directly determined by Knietsch (11). However, this does not necessarily confirm the values at lower pressures. The data obtained in the current investigation could not be

tested in this way, because the vapour pressures were seldom greater than 100 mms. Hg.; their validity could, therefore, only be inferred from the internal consistency and reproducibility. The results obtained for the vapour pressure of water (p. 24) provide a check on the absence of gauge errors and the general validity of the method.

Heats and Entropies of Vaporisation

Heats and entropies of vaporisation are obtained when the temperature dependence of vapour pressure is analysed by the Clausius-Clayperon equation, which for an ideal vapour may be written

$$R \frac{d \ln p}{d\, 1/T} = -\Delta H = -T.\Delta S \qquad \text{(III)}$$

where ΔH and ΔS are the molar heat and entropy of vaporisation, respectively.

Throughout the temperature and concentration range under consideration, the approximation that the dissolved sulphur trioxide exists as disulphuric acid appears sufficiently good and the system may be discussed in terms of the components (a) liquid phase, $H_2S_2O_7$ and H_2SO_4 and (b) vapour phase, SO_3. Applying the Clausius-Clayperon equation to the experimental results (p. 23) should give linear log p vs. 1/T plots of

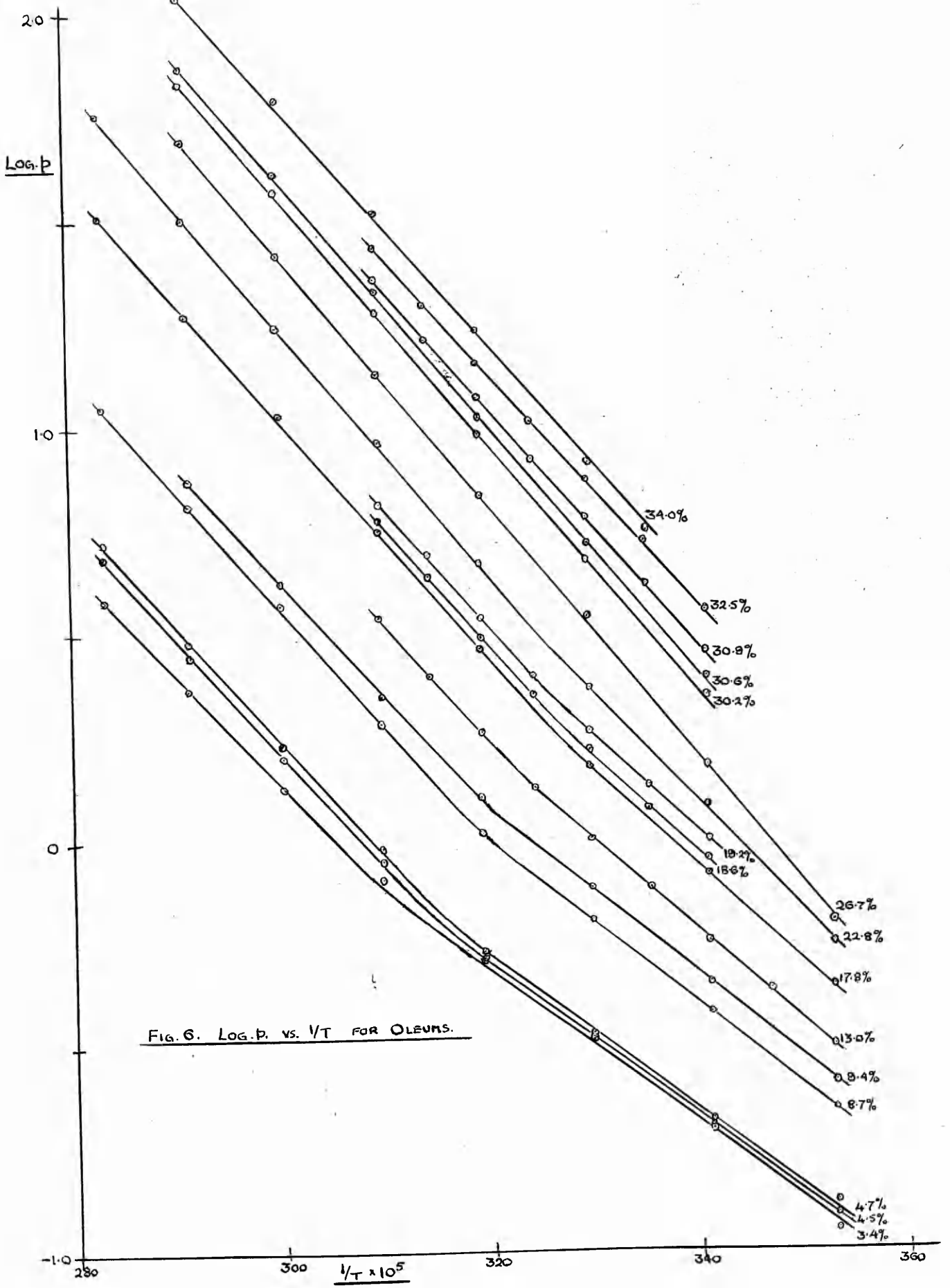


FIG. 6. LOG. p. VS. 1/T FOR OLEUNS.

slope $\Delta H/2.303R$, for oleums of constant composition, the experimental ΔH being the change of heat content when

$$H_2S_2O_7\left\{\begin{matrix}\text{Solution,}\\ \text{in x\% medium}\end{matrix}\right\}=H_2SO_4\left\{\begin{matrix}\text{in x\%}\\ \text{medium}\end{matrix}\right\}+SO_3(\text{vapour})$$

Fig. 6 shows the experimental data plotted in this form and the values of ΔH derived from the graphs are given in Table 4. In the temperature interval 10-80°C, ΔH is independent of temperature for the stronger oleums ($>25\%$ "free" SO_3). In the case of the weaker oleums the data seperate into two regions, the value of ΔH at the higher temperatures being the same as that found with the stronger oleums, whilst at the lower temperatures ΔH is up to 30% smaller. Similarly, at low temperatures the entropy of vaporisation is less for dilute oleums than for concentrated, while at the higher temperatures ($>50°C$) ΔS is independent of composition (Table 4).

Qualitatively similar results (p. 6) were recorded by Miles (14), ΔH for the higher temperatures changing from 12.1 to 12.5 kcals with increase in concentration from 6.4 to 32.3% "free" SO_3. Miles did not analyse the results further because the change of slope of the log p vs. 1/T function occured at pressures of a few mms Hg. only, and Miles did not consider his results quantitative below a pressure of 10 mms. Hg.

Table 4. Heats and Entropies of Vaporisation at 25° and 60°C.

% SO_3	ΔH_{333}	ΔH_{298}	ΔS_{333}	ΔS_{298}
3.4	12.3	8.8	37.0	29.6
4.5	13.1	9.1	39.4	30.6
4.7	13.5	9.2	40.5	30.9
8.7	13.0	9.2	39.1	30.9
9.4	13.2	9.5	39.7	31.9
13.0	13.3	10.0	39.9	33.6
17.8	13.5	11.5	40.5	38.6
18.6	13.4	11.1	40.2	37.2
19.2	13.3	11.4	39.9	38.3
22.8	13.1	11.2	39.4	37.6
26.7	13.7		41.1	45.9
30.2	13.6		40.8	45.6
30.6	13.4		40.2	45.0
30.9	13.0		39.1	43.6
32.5	12.8		38.5	43.0
34.0	13.0		39.1	43.6

ΔH in kilocalories.

ΔS in calories degrees^{-1}.

The vapour pressure data of du Pont (13) give values of ΔH decreasing from 18.1 to 13.2 kcals. over the same concentration range, whilst the data of McDavid (12) are not amenable to this treatment, without interpolation, since composition and SO_3 pressure were both experimental variables, only the temperature being constant.

The existance of the anomaly of low values of ΔH and ΔS for dilute oleums at low temperatures is not in agreement with the calorimetric work of Miles, Niblock and Smith (25) who measured the heat developed when liquid sulphur trioxide was added to oleum. They made the reasonable assumption that the heat of vaporisation of SO_3 from oleum is equal to the heat of vaporisation of liquid SO_3 (10.5 kcals.) plus the partial molal heat of mixing liquid SO_3 with oleum. These thermal measurements give ΔH (at 30°C) as 14.5 kcals. over the concentration range 1-30% SO_3 while the present vapour pressure data give values which are ~4 kcals. smaller in the most dilute oleum. There exists a difficulty in the thermal experiments, as follows; liquid sulphur trioxide is chemically inhomogeneous, probably being a mixture of monomer, cyclic trimer and at least one other polymer (26, 27), and the colligative properties depend upon the proportion of the components. Equilibrium between the

components is reached very slowly; moreover, the rigid exclusion of water further retards the attainment of equilibrium (26). Miles, Niblock, and Smith included distillation over P_2O_5 in their preparation of SO_3 which would inhibit the establishment of equilibrium, and it may be significant that, the more intensive the drying, the higher they found the value of ΔH. The value of 10.5 kcals. for the heat of vaporisation of liquid SO_3 was the value obtained by Miles from vapour pressure measurements (14), and compares with the values of 10.0–10.4 kcals. found by other workers (28, 29, 30).

Those samples of SO_3 which had been most intensively dried yielded values of ΔH which agreed with experimentally measured heats of evaporation (Miles, Niblock and Smith (25)). The latter were obtained by finding the heat required to maintain the temperature ($\sim 30^\circ C$) of an oleum constant during the evaporation of a known amount of SO_3. They were not determined for oleums of $<20\%$ SO_3 because the vapour pressure was too low and evaporation very slow. In the region 20–30% SO_3 it is possible that the measured quantities are not equilibrium heats of evaporation but correspond to an energy of activation for evaporation (or some compromise quantity). This may account for the results being higher than those

from vapour pressure data for this region, there being a decrease in the discrepancy with increasing concentration, but it is necessary to suppose that the agreement in the same region between the two series of thermal measurements is fortuitous. However, it seems most unlikely that any treatment of the liquid SO_3 by Miles could obscure the maximum in ΔH observed in the present investigation, while it is disturbing that the values of ΔH_{298} (Table 4) suggest that liquid SO_3 should dissolve endothermically in dilute oleums (3-5% SO_3) at room temperatures.

However, in the remainder of the discussion it will be assumed that the values of ΔH deduced from the vapour pressure of dilute oleums at low temperature (Table 4, column 3) are real, and a plausible explanation is outlined below. To account for the anomaly, the effects of equilibria must first be considered. These equilibria arise from dissociation of disulphuric acid,

$$H_2S_2O_7 \rightleftharpoons H_2SO_4 + SO_3 \qquad \text{(II)}$$

from the ionisation of disulphuric acid in solution,

$$H_2S_2O_7 + H_2SO_4 \rightleftharpoons HS_2O_7^- + H_3SO_4^+ \qquad \text{(IV)}$$

and from the formation of polysulphuric acids,

$$H_2S_2O_7 + H_2S_2O_7 \rightleftharpoons H_2S_3O_{10} + H_2SO_4 \qquad \text{(V)}$$

Association of SO_3 in the gas phase is ruled out by

direct evidence from vapour density determinations (31). The effect of excess H_2SO_4 would be to assist (IV) to the right and (II) and (V) to the left, thus (IV) should be more apparent in dilute oleums and (II) and (V) in concentrated oleums. Therefore only (IV) might explain the low temperature anomaly, although (II) and (V) can probably account for the fall in ΔH at the highest concentrations (Table 4), which was observed by Miles (14) to continue at greater concentrations. The use of (IV) to explain the anomaly raises the following diffuculty. If this is the correct explanation then the ionisation of disulphuric acid must be endothermic, which is possible; but increasing the temperature would then increase the degree of ionisation and would further lower ΔH, whereas ΔH actually rises at quite moderate temperatures. It appears therefore that attempts to explain the anomaly using equilibrium (IV) must be abandoned.

The most plausible alternative is to attribute changes in ΔS to changes in the entropy of solvation in the liquid phase. Viscosity (32), dielectric constant (cfr. Part 2), X-ray diffraction (33), and negligible vapour pressure (34) all show that pure H_2SO_4 is a hydrogen-bonded liquid possessing a large degree of local structure. This structure is known to be broken down by

excess of the stoichiometric component H_2O (33) and must also be broken by a stoichiometric excess of SO_3, and by rising temperature. Dilute oleums at low temperatures will possess much of the sulphuric acid structure, with local deformations due to disulphuric acid molecules. The latter can be described as possessing a structure-breaking influence on the sulphuric acid medium, that is they decrease the order and increase the entropy of the system. Consequently the partial molal entropy of vaporisation, ΔS, is smaller than in cases where the structure-breaking entropy does not have to be considered. In strong oleums where H_2SO_4 and $H_2S_2O_7$ molecules are present in the same general order of magnitude there is no structure in the previous sense and no contribution to the entropy of vaporisation from the structure-breaking entropy (Table 4, column 5, last six concentrations). Similarly, increasing the temperature will destroy the structure of the dilute oleums, and at an elevated temperature the entropy of vaporisation is found to be independent of composition (Table 4, column 4).

PART II.

THE DIELECTRIC DISPERSION OF SULPHURIC ACID

INTRODUCTION

The method of measuring the low frequency dielectric properties of a substance is to incorporate the material between two electrodes to form a condenser, and then to measure the capacity upon a capacity bridge or by inclusion as part of a resonant circuit. This method is not applicable to substances having high electrical conductivity, since a condenser incorporating such a material as the dielectric is effectively shunted by a low resistance which damps the response of the measuring circuit so that the point of balance or resonance is practically undiscernable. The dielectric properties of anhydrous formic acid (specific conductivity = 6×10^{-5} ohms^{-1} cm.$^{-1}$) were determined by this method (35), but the conductivity of this medium is about the highest permissible.

The dielectric properties of a medium may also be determined from its electromagnetic wave properties. Although Drude (36) applied this principle by using waves guided along transmission lines ("Lecher" lines) at frequencies of the order of 10^8 cycles/second produced by "spark" oscillators, the lack of suitable equipment prevented any wide-spread applications of this method. Drude's method was to measure the properties of the wave

on lines immersed in the medium.

The rapid technical development made during the last decade and a half in the "very high frequency" and "microwave" regions of the radio spectrum has necessitated a knowledge of dielectric properties at these frequencies, and suitable measuring techniques have been evolved. Several of these have the advantage that they may be applied to "lossy" materials including those with high conductivity (e.g. concentrated aqueous solutions of electrolytes, Collie et al. (37)) and have therefore been applied in the present work to a study of anhydrous sulphuric acid.

Walden (38), used a method developed by Drude to carry out measurements on a large number of substances at frequencies of ca. 4×10^8 cycles/second. The method consisted of measuring the resonant length of a line shunted by a condenser filled with the medium, the dielectric constant being interpreted from a calibration, of length vs. dielectric constant, made with substances of known dielectric constant. From the experimental details, the exact meaning of the result ($\epsilon > 84$) for sulphuric acid is not evident, because it is not clear that account has been taken of the dispersion or the effect of the electrolytic conductivity. Thus the

existing datum relating to sulphuric acid is very unsatisfactory.

MEASUREMENT OF DIELECTRIC CONSTANTS AT VERY HIGH FREQUENCIES

Dielectric properties at very high frequencies (39, 40) may be determined by :-

(a) The Resonance Method, in which the material is incorporated in a waveguide resonator, from the dimensions of which, at resonance, the dielectric constant may be determined. This method suffers the same limitations as the low frequency method, namely that the response is damped out by "lossy" dielectrics (p. 34).

(b) The Reflection Method, in which the "standing wave" pattern resulting from the interference between the incident and reflected waves from a sample of dielectric is analysed. This method has been widely used with low loss materials when the effect of the sample length on the reflected waves may be easily studied. It also simplifies with very "lossy" materials ($\tan \delta = \epsilon''/\epsilon' > 2$), when the equivalent of an infinite length of dielectric may be readily obtained, the reflected wave being solely that from the air-dielectric interface.

(c) The Transmission Method, in which the phase change and attenuation of the wave in the medium are determined.

Methods (b) and (c) may be used with guided waves or with free-space radiation. The latter is

sometimes convenient when the material is available as a sheet or at frequencies of the order of 25,000 Mcs/second when probes introduce difficulties, but the use of guided waves has been more extensive.

The high electrolytic conductivity of anhydrous sulphuric acid (specific conductivity ~ 0.01 ohms^{-1} cm.$^{-1}$) precluded the use of the resonance method. It also precluded the use of the first of the reflection methods since the high attenuation made the reflected wave from the back of the sample very weak, compared to the incident wave and the wave reflected from the face of the sample. The second of the reflection methods has the disadvantage that the position of the interface, which is required for the calculation, is somewhat uncertain owing to the meniscus. Transmission methods on the other hand are particularly suitable for a dielectric of high loss, because the attenuation in the sample automatically achieves the necessary isolation of the two sides of the apparatus. Measurements at 1-5 metres were made by methods depending upon transmission in a co-axial waveguide.

THE TRANSMISSION METHOD FOR MEASUREMENT OF DIELECTRIC CONSTANTS

Theory of the Method

The dielectric constant (or permittivity) ϵ of a medium can be determined from the electromagnetic wave properties of the medium. These properties may be defined in terms of two parameters, the intrinsic impedance, and the propagation coefficient. The former, with Fresnel's Equations, determines the reflection and transmission at the boundary of the medium, while the latter determines the properties of the wave within the medium.

Considering an imperfect dielectric medium of true permittivity ϵ', permeability μ, and specific conductivity σ, in which exists an electromagnetic field varying harmonically with time, then Maxwell's Equations take the form:-

$$\text{Curl } \mathcal{E} = -i\omega\mu\mathcal{H} \qquad \text{Curl } \mathcal{H} = \frac{4\pi\sigma}{c^2}\mathcal{E} + \frac{i\omega\epsilon'}{c^2}\mathcal{E} \qquad \text{(VI)}$$

where $\mathcal{E}$ and $\mathcal{H}$ are the complex field vectors, $\mathcal{E}=Ee^{i\omega t}$, $\mathcal{H}=He^{i\omega t}$, $\omega=2\pi\times$ frequency (f), c is the velocity of light, and all quantities are in e.m. c.g.s. units except ϵ' and μ which are in e.s. c.g.s. units. This makes ϵ' and μ dimensionless, and equal to their values relative to free

space for which μ and ϵ' are unity.

For a plane electromagnetic wave in which the "yz" plane is taken as the equiphase surface, then $\mathcal{E}_x$ and $\mathcal{H}_x$ must be zero and Eqns. (VI) reduce to

$$\frac{\delta \mathcal{E}_z}{\delta x} = i\omega\mu \mathcal{H}_y \qquad \frac{\delta \mathcal{H}_y}{\delta x} = -\left(\frac{4\pi\sigma + i\omega\epsilon'}{c^2}\right)\mathcal{E}_z \tag{VII}$$

and eliminating $\mathcal{H}_y$ gives

$$\frac{\delta^2 \mathcal{E}_z}{\delta x^2} - i\omega\mu\left(\frac{4\pi\sigma + i\omega\epsilon'}{c^2}\right)\mathcal{E}_z = 0 \tag{VIII}$$

The solution of Eqn. (VIII) is $\mathcal{E}_z = Ee^{-\gamma x}$ (IX)

where E may be taken as real, and where

$$\gamma = \sqrt{i\omega\mu\left(\frac{4\pi\sigma + i\omega\epsilon'}{c^2}\right)} = \alpha + i\beta \tag{X}$$

The quantity γ is called the "propagation constant" of the wave, its real part α being the "attenuation constant" and the imaginary part β being the "phase constant". α determines the rate of amplitude change of the wave whilst β determines the rate of phase change, their units being nepers*/unit length, and radians/unit length, respectively.

* Two powers P_1 and P_2 are said to differ by N nepers when $P_1/P_2 = e^{2N}$ or $1/2 \ln P_1P_2 = N$.

From Eqn. (X)

$$\alpha + i\beta = i\frac{\omega}{c}\sqrt{\mu}\sqrt{\epsilon' - i\frac{4\pi\sigma}{\omega}}$$

$$\simeq i\frac{\omega}{c}\sqrt{\mu}\sqrt{\epsilon' - i\frac{2\sigma}{f}}$$

$$= i\frac{\omega}{c}\sqrt{\mu}\sqrt{\epsilon' - i\epsilon''} \qquad = i\frac{\omega}{c}\sqrt{\mu\bar{\epsilon}} \qquad \text{(XI)}$$

where $\epsilon' - i\epsilon'' = \bar{\epsilon}$ is the equivalent complex permittivity of the medium, ϵ'' is the dielectric loss factor and $\epsilon''/\epsilon' = \tan\delta$ (δ = dielectric loss angle).

Considering non-magnetic materials for which $\mu = 1$, Eqn. (XI) may be solved for α and β giving:-

$$\alpha = \frac{\omega}{c}\left[\frac{\bar{\epsilon} - \epsilon'}{2}\right]^{1/2} \qquad \beta = \frac{\omega}{c}\left[\frac{\bar{\epsilon} + \epsilon'}{2}\right]^{1/2} \qquad \text{(XII)}$$

$$\left(\alpha = \frac{2\pi}{\lambda_o}\left[\frac{\bar{\epsilon} - \epsilon'}{2}\right]^{1/2}\right) \qquad \left(\beta = \frac{2\pi}{\lambda_o}\left[\frac{\bar{\epsilon} + \epsilon'}{2}\right]^{1/2}\right)$$

or for ϵ' and ϵ'' giving:-

$$\epsilon' = \frac{\beta^2 - \alpha^2}{(\omega/c)^2} \qquad \epsilon'' = \frac{2\alpha\beta}{(\omega/c)^2} \qquad \text{(XIII)}$$

$$\left(\epsilon' = \frac{\beta^2 - \alpha^2}{(2\pi/\lambda_o)^2}\right) \qquad \left(\epsilon'' = \frac{2\alpha\beta}{(2\pi/\lambda_o)^2}\right)$$

Since c = wavelength (λ_o) x frequency (f), the term ω/c in Eqns. (XII) and (XIII) may be replaced by $2\pi/\lambda_o$ (where λ_o

is the free space wavelength of a wave of angular velocity ω), leading to the alternative forms shown in parentheses. This is a practical convenience since it is usually sufficiently accurate (and easier) to measure the wavelength than the frequency.

In the foregoing the imperfect dielectric has been treated as having a conduction current in time phase with the applied field and a displacement current in phase quadrature, the former being expressed in terms of a loss factor $\epsilon''_{TRUE} = \frac{2\sigma}{f}$ (Eqn. (XI)). If the dielectric is also an electrical conductor, this would contribute to the conduction current and hence may analogously be expressed as a loss factor $\epsilon''_{COND} = \frac{2K}{f}$ (where K = specific conductivity in e.s. units) and thus the measured loss factor $\epsilon''_{OBS.}$ would be given by

$$\epsilon''_{OBS} = \epsilon''_{TRUE} + \epsilon''_{COND} = \epsilon''_{TRUE} + \frac{2K}{f} \qquad \text{(XIV)}$$

The legitimacy of expressing the ionic conductance as a loss factor in this manner has been justified by the determinations made by Cooper (41) and Turner (42) on aqueous solutions of electrolytes. These measurements show that outside the dispersion region the difference between the measured loss factor and that calculated on the above assumption is within the experimental error.

In their work on water and concentrated aqueous electrolyte solutions, Collie et al.(43, 37) have used this assumption at frequencies up to ca. 25,000 megacycles/second without introducing any obvious error.

Principles of the Measurements

In the previous section it has been shown that the dielectric properties and the ionic conductivity of a medium may be expressed as a true dielectric constant and a dielectric loss factor and that the two latter may be translated into a complex propagation constant for the passage of a plane electromagnetic wave through the medium. Therefore determination of the components of the propagation constant, the attenuation and phase constants, together with a knowledge of the normal specific conductance, would make it possible to evaluate the true permittivity and loss factor of the material.

In the normal mode of operation of a co-axial transmission line the electromagnetic wave is purely transverse (plane), thus the attenuation and phase constants, may, in essence, be determined by measuring the loss in power and change in phase produced by inserting a sample of the material in the space between the conductors.

(a) Measurement of the Attenuation Constant

A wave travelling along the line from the generator, upon reaching the interface A (Fig. 7) between the air and dielectric suffers partial reflection. The remainder, passes through the dielectric, undergoes a similar experience at the second interface B, and a part appears in the short circuited length (BC) of air-filled line. The section BC contains a device (M), for measuring the power-level (or a function thereof), which appears in it. If the length x (AB) is sufficiently great that after this passage the reflected wave reaching the first interface (P_B) is negligible compared to that exciting the termination element (P), then assuming P_o is the power entering the first interface, the power exciting the terminating element is proportional to* $P_o e^{-2\alpha x}$ Thus the variation of power with x, provides a measurement of the attenuation constant, since

$$\frac{d \ln P}{dx} = 2\alpha \text{ (nepers/cm.)} \qquad \text{(XV)}$$

or in the usual practical units

$$\frac{d \log P}{dx} = \alpha \text{ (decibels}^{\dagger}\text{/cm.)}/_{10}. \qquad \text{(XVI)}$$

* From Eqn. (IX), considering amplitude only $E = E_o e^{-\alpha x}$ i.e. $E^2 = E_o^2 e^{-2\alpha x}$ and for a constant impedance $E^2 \propto P$, thus $P = P_o e^{-2\alpha x}$.

† 1 neper = 8.686 decibels.

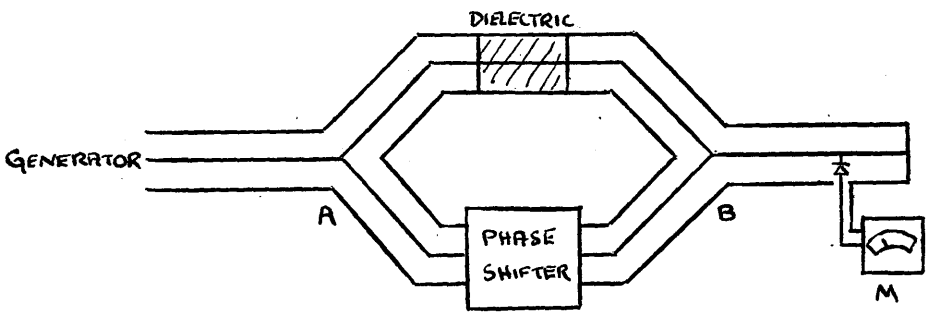


FIG. 8.

This method is particularly applicable to "lossy" liquid dielectrics, since the condition concerning the length (that the reflected wave within the dielectric is completely absorbed) is readily attained, and has been employed by Turner (42) for measurements on water and aqueous NaCl solution, and by Abadie (44) for water, both employing wavelengths of the order of 10 cms. in co-axial waveguides.

(b) Measurement of Phase Constant

The phase constant β is obtained by a interferometric method. The power from the generator is divided (at A, Fig. 8) through the two branches of the circuit and recombined (at B) at the input to a short circuited element containing a device (M) for monitoring the power. The power appearing in the terminating element will depend upon both the relative power levels and phases of the waves at the point of recombination, being a minimum when the phase difference is $(2n+1)$ radians (where n is integral). Thus if the phase of the wave in one branch can be changed by a measurable amount to maintain this condition as the length of the dielectric is varied then a method of measuring β is available.

Practically, it is necessary to avoid interaction between the two sides by introducing a

considerable degree of attenuation in each branch. The use of a sufficient length of "lossy" dielectric provides this in one branch, or an attenuator must be placed before a low loss specimen. A convenient linear phase reference is obtained by picking up, on a probe, a portion of the power in a length of co-axial line terminated in a matched load, and this automatically introduces the necessary isolating attenuation in this branch. Adjustment of the probe penetration is used to compensate the variation in attenuation with sample length, so that the power level of the waves at the point of recombination can be made equal, thus maintaining the condition of maximum sensitivity for adjustment of the reference phase.

If the length of the dielectric sample is increased by Δx, and Δl is the shift of the probe to restore the phase opposition, then the shift Δl is equivalent to a phase change of $2\pi.\Delta l/\lambda_o$ radians, since the phase of a wave changes by 2π radians over a distance of one wavelength (λ_o). A similar phase change has occured in the length Δx of sample, thus

$$\beta = \frac{2\pi.\Delta l}{\lambda_o.\Delta x} \text{ (radians/cm.)} \qquad \text{(XVII)}$$

When the phase difference is zero or $2n\pi$, the power in the monitoring device is a maximum, but this

criterion is never used for measurements due to errors arising from reflections.

This method has not been widely applied to dielectric measurements although it is the method frequently applied to the measurement of the phase pattern of free space radiation (40). Robertson (45) has evolved a more complex system using this principle, for the measurement of the phase change produced by waveguide elements at 4,000 Mcs/second, in which the need for equalising the power level in the two branches is unnecessary.

Although both the methods outlined above were developed in connection with measurements at frequencies of the order of 3,000 Mcs/second and greater, they are also theoretically applicable to measurements at lower frequencies. In the work described herewith, they have been used at frequencies in the region 60-300 Mcs/second.

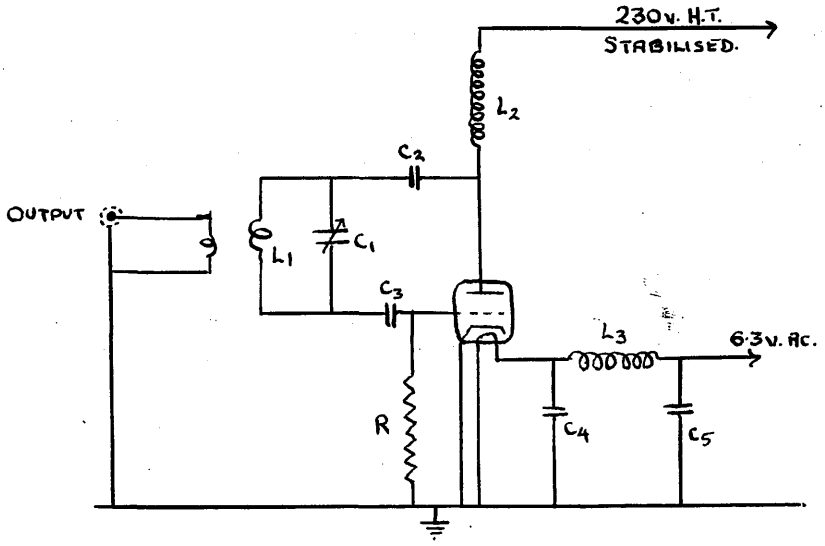


FIG. 8. CIRCUIT DIAGRAM OF OSCILLATORS

	1-2 metres	3-5 metres
C_1	32pfd. Split-stator Variable Condenser	30pfd. Variable Condenser
L_1	9cms. 16S.W.G. Copper Wire	6 turns, 16S.W.G. Copper Wire 1.5cm. I.D.
L_2 and L_3	Radio-frequency Chokes	
C_2	3-30pfd. Trimmer Condenser	
C_3	25pfd. Condenser	
C_4	300pfd. Condenser	
C_5	100pfd. Condenser	
R	20,000ohms Resistor	

EXPERIMENTAL

Apparatus

(a) Oscillators

150-300 Mcs/second:- The triode oscillator (Mullard RL.18 (EC.53)) in a surplus Air Ministry Test Set, Type 83, was converted to continuous operation and provided with a stabilised anode supply. The circuit is shown in Fig. 9. The output power was picked up by a loop constructed from a 75 ohm carbon resistor and carried by flexible co-axial cable (Uniradio 21) to the rest of the apparatus.

60-100 Mcs/second:- This oscillator was similar to the above, with suitable modification of components. The output power was picked up by one turn of 16 S.W.G. tinned copper wire and carried away by co-axial cable.

Both these oscillators proved in use to give outputs which were stable with regard to power and frequency.

(b) Cells

The two cells employed are both lengths of telescopic co-axial line, shown diagrammatically in Fig. 10. One was constructed with a copper outer conductor of

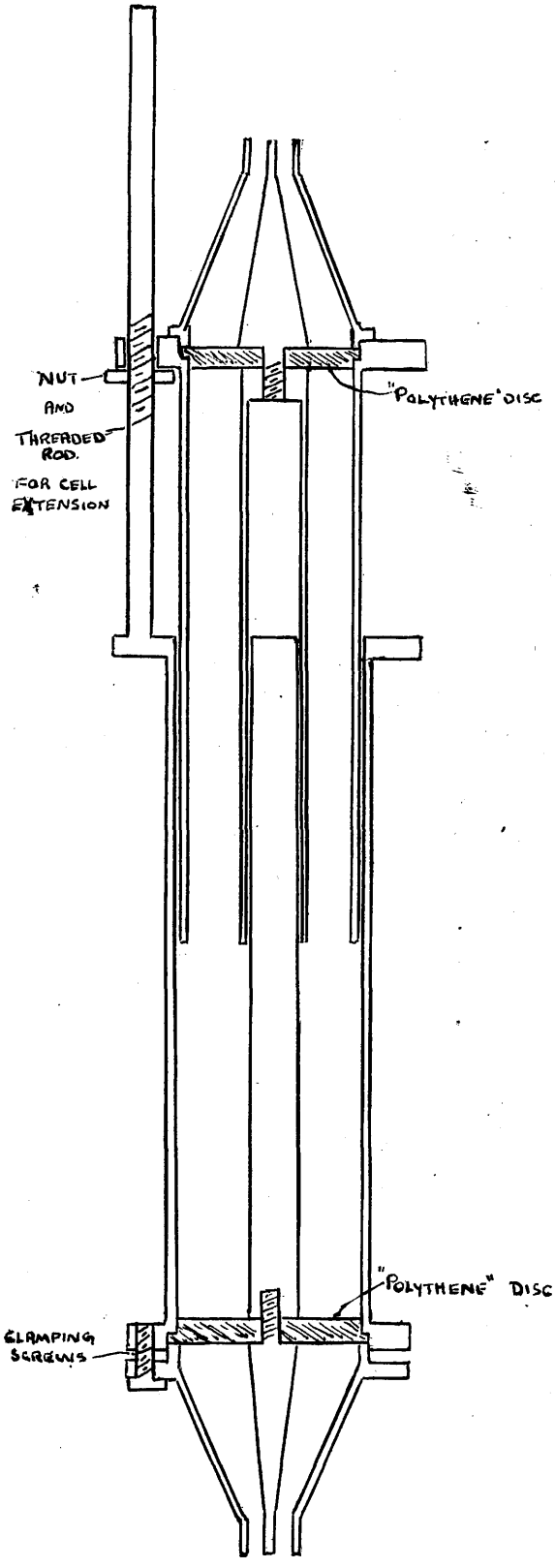


FIG. 10. DIAGRAM OF CELLS.

internal diameter 4.43 cms. and a brass inner conductor of diameter 1.28 cms. for the 15 cm. long fixed part. The surfaces of the conductors of this part of this cell were gold plated to prevent corrosion by the acid. The movable part was made from a copper outer and brass inner conductor of suitable dimensions.

The second was constructed with an outer conductor of 3.78 cms. internal diameter and an inner conductor of 1.28 cms. diameter, both of stainless steel and 30 cms. long. The movable part was made from brass of suitable dimensions.

The inner conductors were held central by 0.63 cm. thick "Polythene" discs, the construction being such that the disc in the fixed part of the cell formed a liquid-tight seal since this section contained the liquid under investigation. The ends of the cells were fitted with tapering sections which reduced the dimensions to those of a G.E.C. co-axial socket. Smooth and positive extension of the cell was performed by the movement of a broad nut up a fixed threaded rod, the nut bearing against a flange attached to the movable portion. The outer conductor of both movable sections was slotted along its whole length to enable the tip of a burette to be accommodated for addition of the liquid.

(c) Power Detectors

The direct measurement of voltage (E) and current (I) at frequencies much in excess of 10^8 cycles/second is not reasonably practicable since these quantities are dependant upon position of the measuring device in the transmission line and their distribution is affected by the introduction of any measuring instrument. Instead the measurement of power (E x I) is of more use, and is usually performed by absorbing the power in some device (e.g. bolometer or thermistor) which has properties that can be calibrated in terms of power absorbed. Crystal detectors, placed $\lambda/4$ from a short circuit, may be used for the relative measurement of very low power levels, the radio frequency voltage developed across the crystal being rectified and the resultant direct current through the crystal being measured. This current, proportional to E^2, is proportional to the power if the voltage is developed across a constant impedance. The one great advantage of crystals over other devices is the simplicity of the associated equipment, only a suitable meter to measure the crystal current (i) being required. Collie (46) has raised doubts concerning the reliability of crystals and their square law ($i \propto E^2$) characteristic. However it has been shown

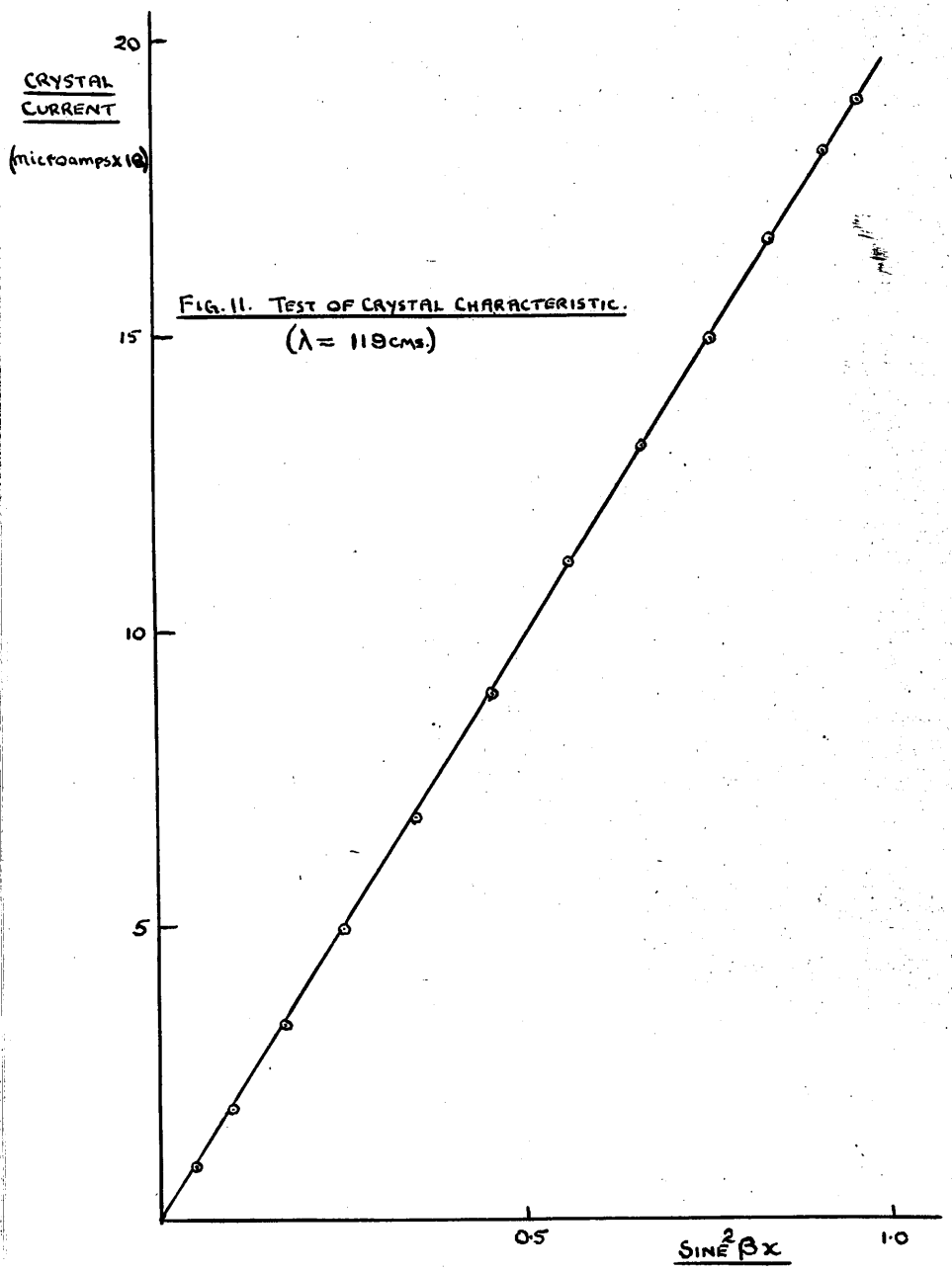


FIG. 11. TEST OF CRYSTAL CHARACTERISTIC.
(λ = 11·9cms.)

by Birks (47) that the square law characteristic is preserved if the crystal current is not more than a few microamperes, although at higher currents it deviates in different degrees depending upon the galvanometer circuit resistance, the optimum value for the latter is about 400 ohms.

In the present work, the crystals were used with a 400 ohms Cambridge "Spot" Galvanometer, which gave full-scale deflection for currents of ca. 1.5 μA. The galvanometer, suitably shunted, was calibrated against a "sub-standard" grade 0-20 microampere meter.

The characteristics of the crystals were tested for square law dependance:- The crystals were inserted in a standing wave detector and the reading of crystal current (i) against detector position were taken over a complete quarter wavelength, the line being terminated in a short circuit. The voltage distribution over a short-circuited lossless line is given by $V^2 = V_o^2 \sin^2\beta x$, thus if $i \propto V^2$ then a plot of i against $\sin^2\beta x$ should be linear. A typical result is shown in Fig. 11, the crystal obeying a power law of 2 ± 0.02. The square law characteristic was therefore assumed in all experiments ($i \lesssim 2\mu A$).

(d) Crystal Mounts and Line Termination

A quarter-wave termination for wave lengths of a metre, was made from a co-axial line, of 1 cm. diameter outer conductor and 0.45 cm. diameter inner conductor, 30 cms. long (Birks (47)). One end contained a mount for the crystal detector and provision for a co-axial input, whilst the other end was fitted with a moveable short circuiting plunger.

At longer wavelengths a quarter wavelength of line becomes bulky and may conveniently be replaced by the equivalent lumped circuit, comprising an inductance and capacity in parallel. This device was resorted to at wavelengths exceeding a metre and a half. The unit was contained in a screening box provided with a co-axial input, a mount for the crystal detector, and a small variable air dielectric condenser (20 $\mu\mu$fds, max.). Suitable circuit values were made up by the addition of fixed ceramic condensers (when necessary) and inductances wound from 16 S.W.G. tinned copper wire.

(e) Co-axial Line Phase Shifter

This employed a co-axial line having an outer conductor of 4.45 cms. inside diameter, and inner conductor of 1.35 cms. diameter, and a length of 110 cms. The inner conductor, constructed of thin-walled tubing, was

supported at intervals upon five sets of three thin "Perspex" rods, screwed through the outer conductor, at 120° to each other (Birks (47)). These spacing rods have been found to have negligible effect upon the wave in the line. A resistive termination, the impedance of which was equal to the characteristic impedance of the line was made from several small carbon rod resistors in parallel, adjusting until the voltage standing wave ratio was less than 1.05 as measured by a travelling detector. Thus the power level along the line was practically constant and varied only in phase. This power was sampled by a probe, whose depth of penetration was adjustable so that the amplitude of the sampled power could be varied, and whose position along the line could read to 0.1 mm. on a vernier scale.

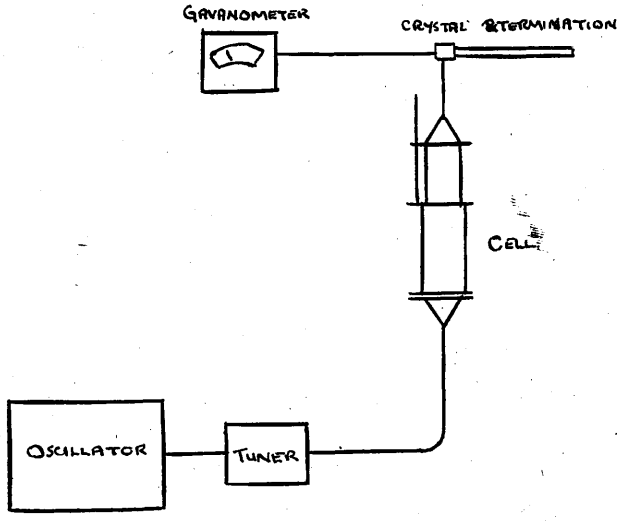
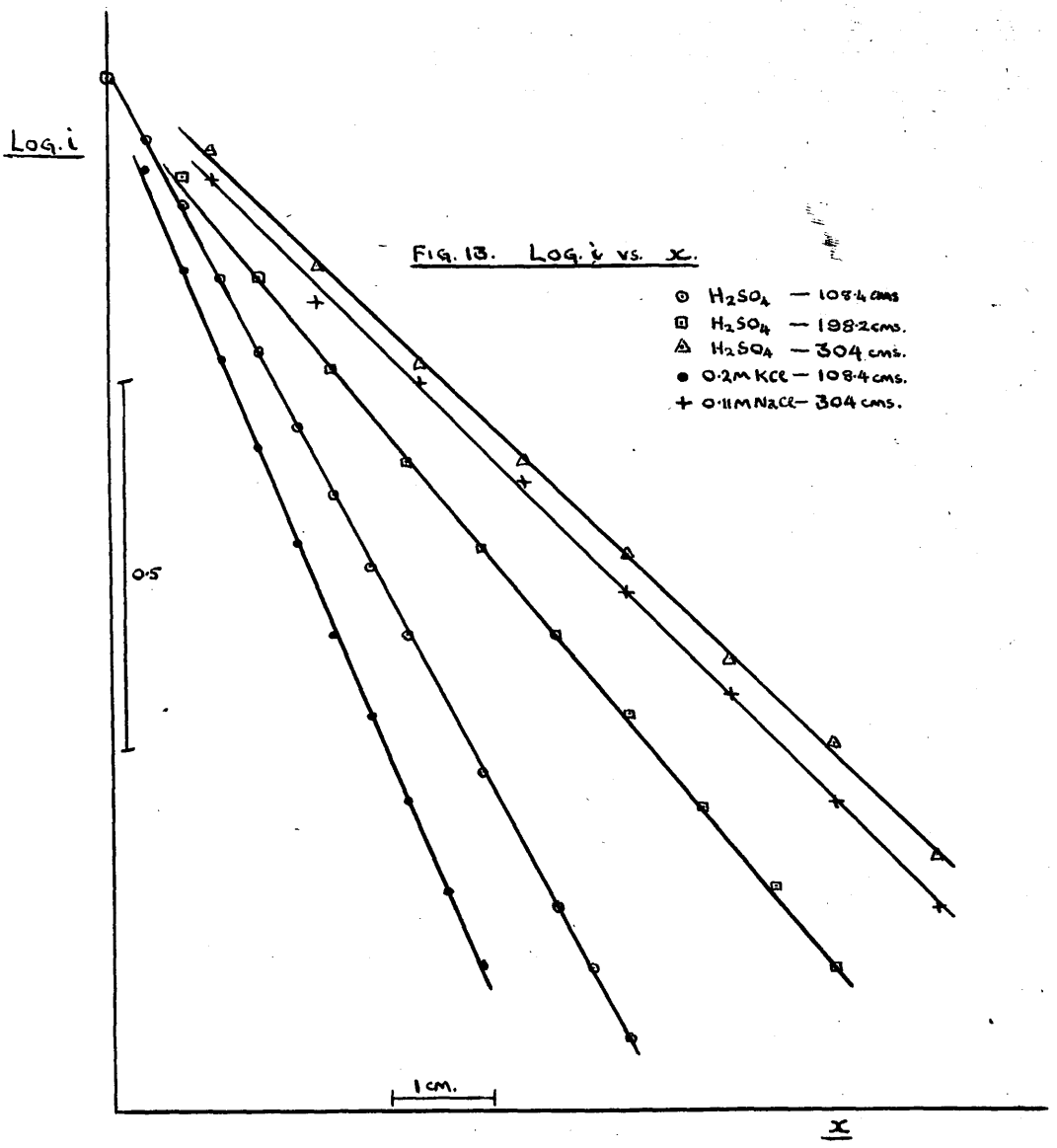


FIG. 12.

Measurement of the Attenuation Constant

The apparatus was arranged as in Fig. 12. The tuner unit consisted of a small variable capacity connected across the line, thus giving control over the electrical length between generator and cell. Sufficient liquid to eliminate the effect of interface reflections (p. 44) was added, a length equivalent to ca. 10 decibels being sufficient, and then the tuner adjusted to give maximum power at the crystal. This latter procedure effects a match between the load and the generator so that the oscillator delivers power to a constant impedance. The termination and length of line between the second interface and the crystal were also adjusted to produce maximum power at the crystal, care being taken to ensure the movable part of the cell was not immersed in the liquid, thus matching the crystal and termination into the liquid-filled length of line and consequently to generator plus load. The power now appearing at the crystal was sufficient to produce nearly maximum galvanometer deflection. Measured quantities of liquid were added from a burette and the length of the cell increased until the galvanometer deflection was maximised, and this deflection noted. In this way the impedance presented by the length of line beyond the


Log. i
FIG. 13. Log. i vs. x.
⊙ H_2SO_4 — 108·4 cms
⊡ H_2SO_4 — 198·2 cms.
△ H_2SO_4 — 304 cms.
● 0·2M KCl — 108·4 cms.
+ 0·11M N_2Cl — 304 cms.
0·5
1 cm.
x

liquid was maintained constant and the crystal current (i) was thus directly proportional to power (p. 50). Changes of power level were observed, in convenient steps, up to a total of 15 to 20 decibels, and the change in length of liquid column (x), to produce this was calculated from the known volume added and the cell dimensions. The results were plotted in the form log i vs. x, which should give a straight line of slope equal to α(dbs/cm.)/10 (p. 44). Typical results are shown in Fig. 13.

Strictly the measured α should also contain a contribution from the cell walls due to the increase in length of cell. However for metals of low resistance, and in the absence of corrosion, the contribution is negligible. This wall "loss" can be calculated (48) and in the present case is of the order 10^{-3} dbs/cm. which is less than 1% of the smallest α (ca. 1 db/cm.) measured.

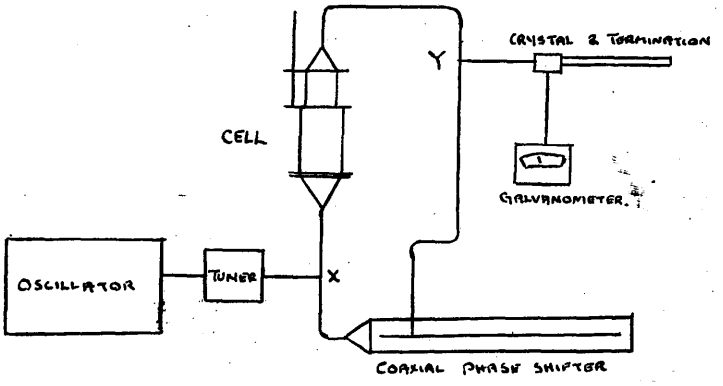
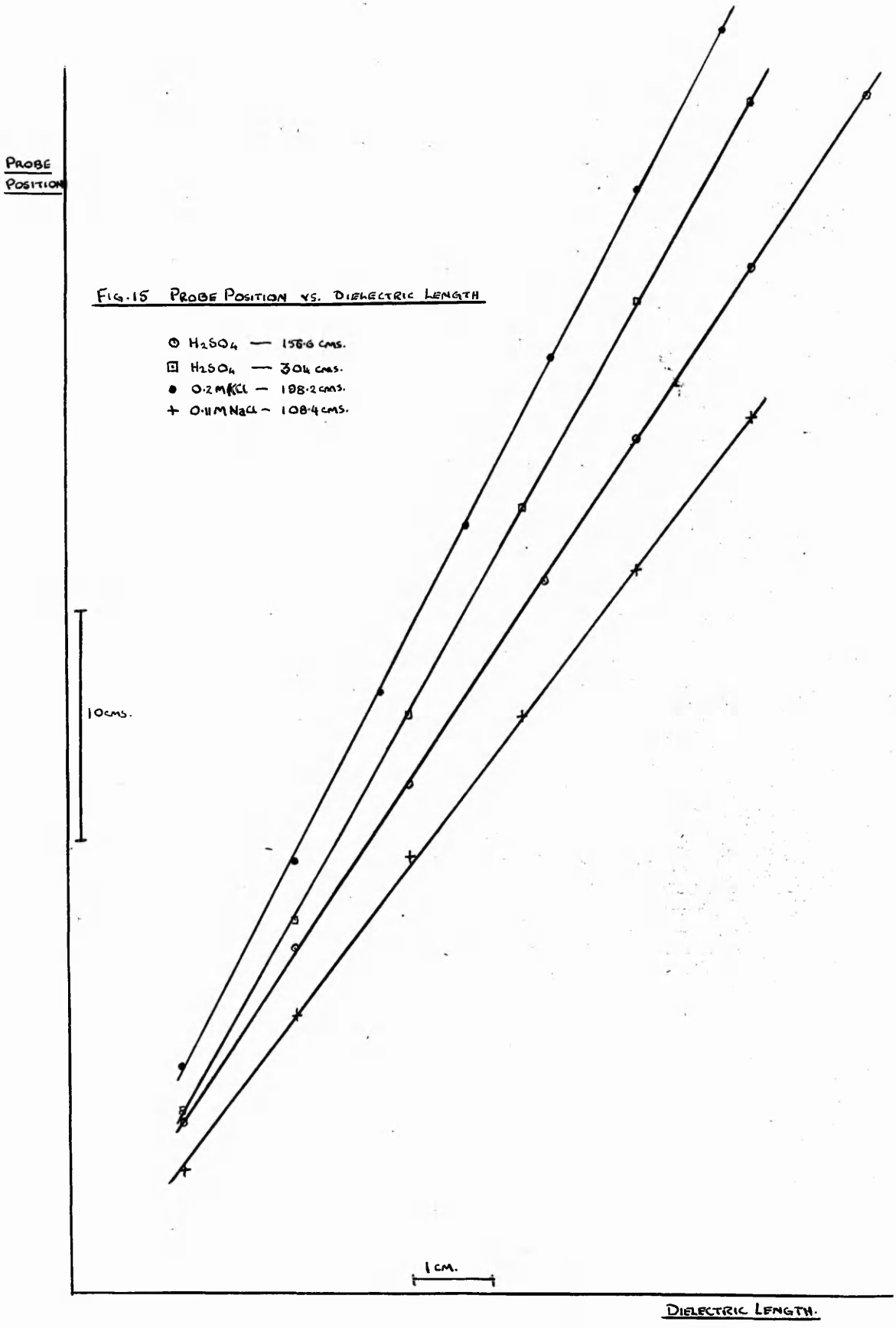

CRYSTAL & TERMINATION
Y
CELL
GALVANOMETER.
OSCILLATOR
TUNER
X
COAXIAL PHASE SHIFTER

FIG. 14.

Measurement of Phase Constant

The apparatus was arranged as in Fig. 14. The various parts were interconnected with co-axial cable, co-axial "T" junctions (X and Y) being employed to divide and recombine the power to and from the two branches. The cable lengths were adjusted such that the probe, crystal and termination, and liquid-filled length of line were approximately matched into Y whilst a deliberate mismatch was introduced between X and the liquid-filled line so that with the minimum necessary attenuation in both branches the power level in each was approximately equal. This allowed an increase in attenuation of each branch of 10-15 decibels whilst still enabling the balance point to be located to better than 1 mm.

Measurements were performed as follows:- An initial attenuating length of liquid (equivalent to ca. 10 dbs.) was placed in the cell and the approximate balance point found and then the power levels balanced by adjusting the depth of penetration of the phase reference probe. The actual balance point was located by plotting the crystal current against probe position, as the probe passed through the balance point, this plot being a parabola symmetrical about an axis passing through the balance point. A measured quantity of the


PROBE POSITION
FIG. 15 PROBE POSITION VS. DIELECTRIC LENGTH
⊙ H_2SO_4 — 158·6 cms.
⊡ H_2SO_4 — 304 cms.
● 0·2 M KCl — 198·2 cms.
+ 0·11 M NaCl — 108·4 cms.
10 cms.
1 cm.
DIELECTRIC LENGTH.

sample was added from a burette, the cell extended by a length equivalent to the increase in liquid depth calculated from volume added and cell dimensions, the approximate balance point located and power equalised by withdrawing the probe. The exact balance point was then located as before. This was repeated several times, until the sensitivity was reduced by the increase in attenuation as mentioned above. The sample length (x) was plotted against balance point of probe (1) and the slope ($\Delta l/\Delta x$) of the resulting linear plot was used in Eqn. (XVII) to obtain the phase constant β (p.46):-

$$\beta = \frac{2\pi . \Delta l}{\lambda_o . \Delta x} \qquad \text{(XVII)}$$

Typical results are shown in Fig. 15.

Measurement of Wavelength

A knowledge of the frequency (f) at which the measurements are being made is necessary, and this can be conveniently determined in terms of the equivalent free-space wavelength (λ_o) since $\lambda_o f = c$ (where c = velocity of light, 3×10^{10} cms/second).

To each oscillator a subsidiary single turn pick-up loop was very loosely coupled and led to a "Lecher" line. This latter comprised two lengths of about 3 meters of 16 S.W.G. tinned copper wire stretched taught and spaced 2.5 cms. apart. A brass short-circuiting bridge could be run along these wires and its position noted on a metric boxwood scale. When this bridge was at a current node the line became resonant, this condition being indicated by a change in anode current of the oscillator or, when the other circuits were connected, by a reduction in the power present at the crystal. The coupling of the "Lecher" line to the oscillator was such that these effects were only just apparent, enabling the node to be sharply located, and since the distance between two consecutive nodes is $\lambda_o/2$, the wavelength may be determined. At the shorter wavelength (ca. 100 cms.) the value of $\lambda_o/2$ could be established to better than a millimetre using several

successive nodes and at the longest wavelength (ca. 500 cms.) $\lambda_0/2$ could be determined to within 2 millimetres from successive measurements of the only two nodes present on the line.

The use of a subsidiary pick-up loop in these measurements enabled the wavelength to be determined whilst the oscillator was under load, and thus eliminated the uncertainty of frequency change produced by loading the oscillator. Measurements of λ_0 with loaded and unloaded oscillators showed that such "pulling" was negligible.

Measurements of Conductivity. (By Dr. J.C. James)

The measurements were carried out in a "U"-shaped cell, with bright platinum electrodes, using a screened A.C. bridge (49), at a frequency of 1,000 to 3,000 cycles/second, the cell being immersed in a thermostat at 20 ± 0.01°C. The cell was standardised using Jones and Bradshaw's 0.1 M and 1.0 M potassium chloride.

Results for Sulphuric Acid

All measurements were carried out in a room whose temperature was maintained at 20 ± 1°C.

Anhydrous sulphuric acid was prepared by reinforcing "Analar" concentrated sulphuric acid with pure oleum (p. 19) to give an acid of minimum conductivity (50), and measurements of the attenuation and phase constants were made at four wavelengths between 1 and 3 metres, the results being shown in Table 5. The specific conductivity, also shown in Table 5, was measured after each experiment to ensure that no significant change had taken place due to the absorption of water, the latter being minimised by leading a stream of dry (P_2O_5) nitrogen into the cell during measurements. This is necessary since the conductivity changes very rapidly with concentration either side of the minimum, but it was found that with the above precautions and with the attachment of a drying tube (P_2O_5) to the top of the burette from which the sulphuric acid was added to the cell, this change was kept less than 2%.

Table 5. Results for Anhydrous Sulphuric Acid.

λ(cms)	α(nepers/cm)	K(ohms^{-1}cm^{-1})	β(rads/cm)	K(ohms^{-1}cm^{-1})	ϵ'	$\epsilon''_{obs.}$	$\epsilon''_{cond.}$	ϵ''_{true}
108.4	0.309	0.0087	0.567	0.0087				
	0.310	0.0088	0.558	0.0088				
	0.310	0.0086	0.568					
	0.327	0.0092						
	0.333	0.0094						
mean	0.318	0.0089	0.564		65	107	58	49
156.6	0.214	0.0086	0.428	0.0095				
	0.213	0.0086	0.428					
	0.215	0.0086						
	0.240	0.0095						
	0.239	0.0092						
mean	0.225	0.0090	0.428		82	120	84	36
198.2	0.191	0.0088	0.364	0.0090				
	0.192	0.0087	0.366					
	0.191							
	0.189	0.0086						
	0.193							
mean	0.191	0.0088	0.365		97	139	104	35
304.0	0.161	0.0085	0.260	0.0094				
	0.155	0.0087						
mean	0.158	0.0089	0.260		100	192	162	30

Results for Aqueous Solutions

All measurements were carried out in a room whose temperature was maintained at 20 ± 1°C.

Measurements of the attenuation and phase constants were made for 0.1 M sodium chloride and 0.2 M potassium chloride solutions at the same frequencies as those for sulphuric acid. These measurements, shown in Table 6, were made partly for their own sake and partly as a check on the apparatus and method since the results can be calculated from the data of Collie (37). The agreement between the experimental and calculated values shows that experimental error is of the order of ± 2%.

Table 6. Results for Aqueous Electrolytes.

Soln.	λ (cms)	found α (nepers/cm)	found β (radians/cm)	found ϵ'	found ϵ''	calculated α (nepers/cm)	calculated β (radians/cm)	calculated ϵ'	calculated ϵ''
0.11M NaCl	108.4	0.213	0.540	76.0	69.5	0.209	0.554	78.5	68.8
		0.214	0.556						
	156.6	0.198	0.410	78.3	99.7	0.196	0.406	78.5	99.1
		0.191	0.400						
	198.2	0.185				0.187	0.397	78.5	126
		0.187							
	304.0	0.171	0.251	78.1	195	0.167	0.249	78.5	192
		0.167							
		0.170							
0.20M KCl	108.4	0.390	0.635	76.5	148	0.384	0.641	78.5	146
		0.389	0.641						
	156.6	0.345	0.500	81.4	215	0.344	0.496	78.5	211
		0.345							
	198.2	0.319	0.425	78.2	271	0.316	0.422	78.5	267
		0.320							
	304.0	0.270				0.270	0.327	78.5	406
		0.272							
		0.270							

DISCUSSION

Dielectric Dispersion

Anomalous dispersion in liquids, that is the decrease in dielectric constant with increasing frequency, was first observed by Drude (36), and was put on a theoretical basis by Debye (51) who represented the effect as a transition from the combined orientation and distortion of the molecules to the pure distortion when under the influence of an electic field.

Van Vleck and Weisskopf (52) have derived the usual Debye expression by considering the resistance of the molecules to rotation as inertial rather than viscous. It is supposed that, after collision, the probability of distribution of a dipolar molecule is distributed in accordance with the Boltzmann Law; then, considering a molecule, at a time t, whose preceding collision was at a time t_o, in a field $E_o \cos\omega t$, the mean moment of the molecule $\bar{m}$, is

$$\bar{m} = \frac{\mu \int_0^{\pi} \cos\psi \exp[\mu E_o \cos\psi \cos(\omega t_o/kT)] \sin\psi \cdot d\psi}{\int_0^{\pi} \exp[\mu E_o \cos\psi \cos(\omega t_o/kT)] \sin\psi \cdot d\psi} \qquad \text{(XVIII)}$$

If it is assumed that the inertia of the molecule is so large that it is stationary between collisions, which is warranted if the frequency of collision is high compared to the molecular rotation frequency, taking only the

lowest terms in the non-vanishing order of E, Eqn. (XVIII) becomes

$$\bar{m} = \frac{\mu^2 E \cos(\omega t_0) \int_0^{\pi} \cos^2\psi \cdot \sin\psi \cdot d\psi}{kT \int_0^{\pi} \sin\psi \cdot d\psi} = \frac{\mu^2 E}{3kT} \Re \exp(i\omega t_0) \qquad \text{(XIX)}$$

where $\Re$ = real part. To obtain the mean moment per mole Eqn. (XIX) must be multiplied by Avogadro's Number N and averaged over the various times of last collision. With random collisions, $(1/\tau)\exp(-\theta/\tau).d\theta$ is the probability that the collision experienced before **t** was in the interval $t-\theta-d\theta$ and $t-\theta$, where τ is the mean interval between collisions.

Thus $$N\bar{m} = \frac{NE\mu^2}{3kT} \Re \frac{1}{\tau} \int_0^{\infty} e^{i\omega(t-\theta)} e^{-\theta/\tau} . d\theta = \frac{NE\mu^2}{3kT} \Re \frac{e^{i\omega t}}{1+i\omega\tau} \qquad \text{(XX)}$$

which is the usual expression of Debye.

The relations of Clausius and Mosotti (51) lead to a molar polarisation, P:-

$$P = \frac{\epsilon-1}{\epsilon+2} \frac{M}{\rho} = \frac{4\pi}{3}\left(N\alpha_D + N\alpha_0\right) \qquad \text{(XXI)}$$

where $\alpha = (\bar{m}/E_0)e^{-i\omega t}$ is the mean polarisability per molecule, subscripts D and O refer to that due to distortion and orientation, respectively.

Thus $$P = \frac{\epsilon-1}{\epsilon+2} . \frac{M}{\rho} = \frac{4\pi N\alpha_D}{3} + \frac{4\pi N \mu^2}{3kT} \frac{1}{1+i\omega\tau} \qquad \text{(XXII)}$$

The liquid may be characterised by the two dielectric constants ϵ_0 and ϵ_∞ which are defined:-

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\,\frac{M}{\rho} = \frac{4\pi N \alpha_D}{3} \qquad \text{(XXIII)}$$

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2}\,\frac{M}{\rho} = \frac{4\pi N}{3}\left(\alpha_D + \frac{\mu^2}{3kT}\right) \qquad \text{(XXIV)}$$

ϵ_∞ thus denoting the value at high frequencies (the optical dielectric constant) and ϵ_0 denoting the static dielectric constant observed for $\omega = 0$ (practically, for low frequencies) and from Eqns. (XXII), (XXIII) and (XXIV) the usual Debye Equation is obtained

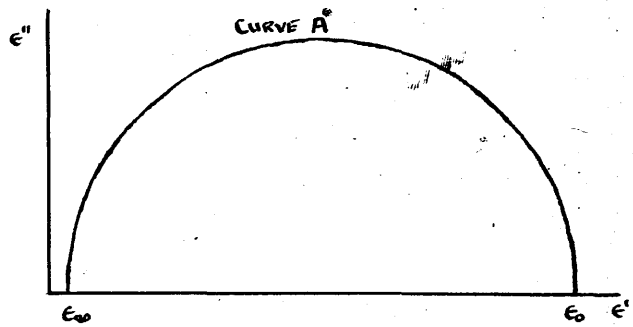
$$\bar{\epsilon} = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(1 + i\omega\tau_0) \qquad \text{(XXV)}$$

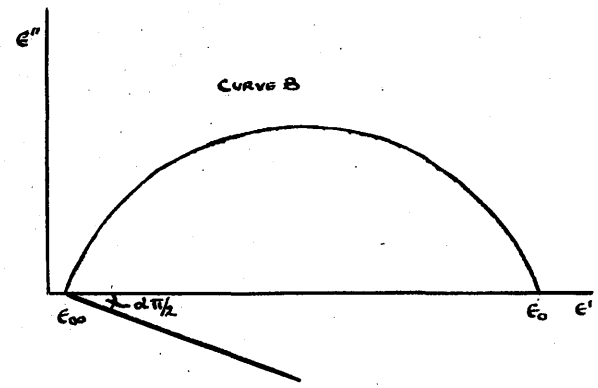
where $\bar{\epsilon} = \epsilon' - i\epsilon''$ is the complex dielectric constant at the angular frequency ω, and τ_0 is a characteristic constant called the relaxation time.

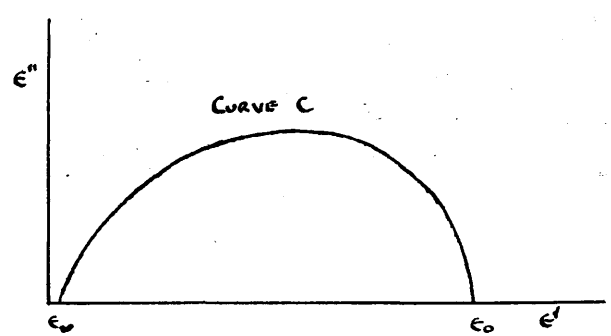
Eqn. (XXV) may be rearranged to give the dependance of the dielectric constant ϵ' and loss factor ϵ'' upon frequency

$$\epsilon' = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(1 + \omega^2\tau_0^2) \qquad \text{(XXVI)}$$

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty)\omega\tau_0/(1 + \omega^2\tau_0^2) \qquad \text{(XXVII)}$$







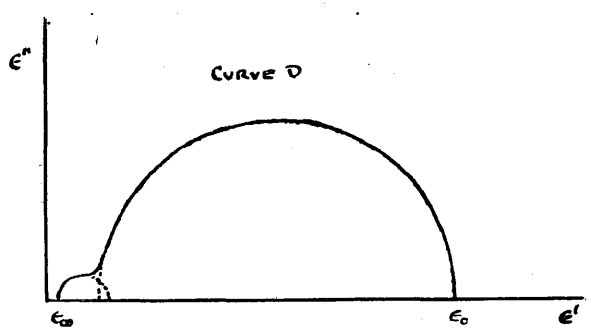


FIG. 16. COLE AND COLE DIAGRAMS

Eqn. (XXVI) and (XXVII) can be combined and written in the form of the equation for a circle

$$\left(\epsilon' - \frac{\epsilon_o + \epsilon_\infty}{2}\right)^2 + \epsilon''^2 = \left(\frac{\epsilon_o - \epsilon_\infty}{2}\right)^2 \qquad \text{(XXVIII)}$$

Since all values must be positive this gives a semicircular plot of ϵ' against ϵ'' whose centre lies on the ϵ' axis with intercepts at ϵ_∞ and ϵ_o on this axis (Curve A, Fig. 16).

If the values of ϵ'' give a semicircle when plotted against those of ϵ', then the data conform to the theory of Debye. Experimentally it is found that the Debye Equation is not universally satisfied, the change of ϵ' from ϵ_∞ to ϵ_o occuring over greater range of frequencies than the theory predicts, and ϵ''_{max} having a lower value than that predicted by Eqn. (XXVII) viz. $\epsilon''_{max} = (\epsilon_o - \epsilon_\infty)/2$. Cole and Cole (53) found that the experimental data commonly fell below the semicircle and could be represented by a circular arc intersecting the abscissa axis at ϵ_∞ and ϵ_o. The centre of curvature of this arc lay below the abscissa axis, and the diameter drawn through the centre and ϵ_∞ made an angle $\alpha\pi/2$ with the abscissa axis (Curve B, Fig. 16). This behaviour is represented mathematically by

$$\bar{\epsilon} = \epsilon_\infty + \frac{\epsilon_o - \epsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \qquad \text{(XXIX)}$$

which differs only from the Debye Equation by the introduction of the empirical constant α, with values between 0 and 1, which is a measure of the distribution of relaxation times. τ is the most probable relaxation time and corresponds to the frequency at which ϵ'' is a maximum.

Cole and Davidson (54) have found a hybrid behaviour for glycerol at low temperatures, locus ϵ' and ϵ'' following an arc plot at the high frequencies but changing to a circular plot at the lower frequencies (Curve C, Fig. 16). They found that this behaviour could be expressed by

$$\bar{\epsilon} = \epsilon_\infty + \frac{\epsilon_o - \epsilon_\infty}{(1 + i\omega\tau)^{1-\alpha}} \qquad \text{(XXX)}$$

where the symbols have the same meaning as for Eqn. (XXIX).

Normally in the interpretation of the data in this manner it is sufficient to take ϵ_∞ as the square of the refractive index for the sodium line, n_D^2. Smyth et al (55) have found, from their measurements on a large number of organic halides, that a more consistant representation of the data was obtained by using a slightly higher value of ϵ_∞ which contains calculated contribution from the atomic polarisation. In general, for polar liquids the empirical value $\epsilon_\infty \sim 3$ may be taken. With polar associated liquids there may be two

overlapping dipolar processes, but the high frequency component is small and contributes very little to the dispersion of the dielectric constant (Curve D, Fig. 16). The high values of ϵ_∞ ($\sim$5.5) for water found by Collie (43) on applying the Debye equations to their experimental results is probably due to this occurence. Latimer (56) however attributes it to an increase in the permanent dipole moment of the molecule arising from an appreciable displacement of the proton along the direction of the hydrogen bond.

The relaxation time (τ) may be derived as follows. Equations (XXVI) and (XXVII) on solution for give

$$\omega\tau = v/u \qquad \text{(XXXI)}$$

where v is the distance between ϵ_o and one experimental point i.e. $v^2 = \epsilon''^2 + (\epsilon_o - \epsilon')^2$ and u is the distance between ϵ_∞ and the same experimental point, i.e. $u^2 = \epsilon''^2 + (\epsilon' - \epsilon_\infty)^2$, and τ is the only unknown. Similarly for the Cole and Cole equation (XXIX)

$$(\omega\tau)^{1-\alpha} = v/u \qquad \text{(XXXII)}$$

where v and u are the same as in Eqn. (XXXI). The absorption is a maximum (ϵ''max) when v/u = 1

$$\text{i.e. } \omega\tau = 1 \text{ or } (\omega\tau)^{1-\alpha} = 1 \qquad \text{(XXXIII)}$$

and since $\omega = \frac{2\pi c}{\lambda}$, substituting for ω in Eqn. (XXXIII)

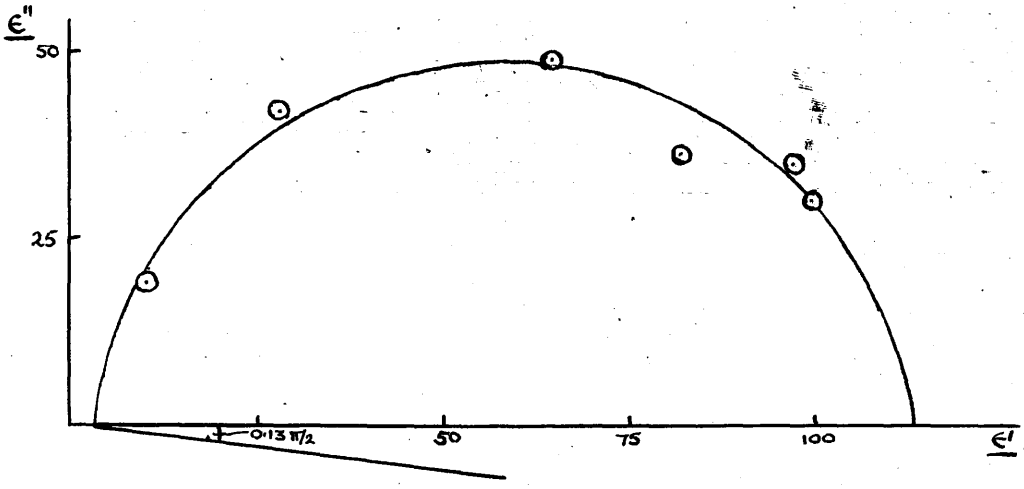


Fig. 17. Cole and Cole Diagram for Sulphuric Acid.

gives

$$\lambda_m = 2\pi c \tau \qquad \text{(XXXIV)}$$

where λ_m is the wavelength at which ϵ'' is maximum.

Figure 17 is the Cole and Cole diagram for sulphuric acid using the results in Table 5, together with unpublished value measured at 10 cms. ($\epsilon' = 10, \epsilon'' = 19$) and 27 cms. ($\epsilon' = 28, \epsilon'' = 42$) by Drs. Brand and James. These results were found to fit best a circular arc plot with intercepts on the ϵ' axis at $\epsilon_\infty \sim 3$ and $\epsilon_o \sim 110$, with the diameter through ϵ_∞ and the centre making an angle $\sim 0.13\,\pi/2$ with the abscissa axis, thus $\alpha = 0.13$. Equation (XXXII), taking the point determined at 108.4 cms., gives for the relaxation time $\tau = 4.6 \times 10^{-10}$ seconds, from which Equation (XXXIV) indicates that is a maximum at a wavelength $\lambda_m \sim 87$ cms.

The Debye theory accounts satisfactorily for the behaviour of gases and dilute solutions of polar molecules in non-polar liquids, but fails for liquids in general since it neglects the interaction between the molecules. Onsager (57) treated a molecule as a spherical cavity, of dielectric constant equal to the square of the optical refractive index (n^2) of the liquid, surrounded by a continuum of liquid of uniform dielectric constant (ϵ_o). He introduced the concept pf a

reaction field which acts upon the dipole as a result of the electrical displacements induced by its own presence and obtained the equation

$$\frac{(\epsilon_o - n^2)(2\epsilon_o + n^2)}{\epsilon_o(n^2+2)} = \frac{4\pi N\mu_o^2}{9kT} \qquad \text{(XXXV)}$$

where μ_o is the permanent dipole moment of an isolated molecule and N is the number of molecules per cc.

The equivalent Debye equation may be obtained by combining Equations (XXIII) and (XXIV), and rearranging:-

$$\frac{3(\epsilon_o - \epsilon_\infty)}{(\epsilon_o + 2)(\epsilon_\infty + 2)} = \frac{4\pi N\mu_o^2}{9kT} \qquad \text{(XXXVI)}$$

where the symbols have the same significance as in Equation (XXXV). The right-hand side can be calculated from values of μ_o obtained either from measurements on the vapour, or, with sufficient accuracy, from measurements made on dilute solutions in non-polar solvents. Using these values of μ_o, the calculated and experimental values of ϵ_o can be compared. It is found that, if one excludes associated substances like water, alcohols, and ammonia, Equation (XXXVI) gives no agreement while Equation (XXXV) gives a rough agreement (58).

Taking $\mu_o = 3.27$, the value found for dimethyl sulphate in dilute solution (59), and $\epsilon_\infty = n^2 = 2.25$,

then Equation (XXXV) gives $\epsilon_o = 38$. Onsager remarks that his optical refractive index should include the "atomic polarisation" due to elastic displacement of the atomic nucleus in the electric field, thus taking the value $\epsilon_\infty = 3$, Equation (XXXV) gives $\epsilon_o = 54$ (cfr. p. 68).

Thus sulphuric acid falls in the same class as water and alcohols, in that the calculated dielectric constant on the theory of Onsager is very much less than the experimental. This is further evidence for the existence of hydrogen bonding in this medium. Kirkwood's treatment of hydrogen bonded liquids (60) cannot be applied in the presence instance due to insufficient structural evidence, in particular the average value of the cosine of the angle between the dipole and one of its neighbours, which is required for the calculation.

GENERAL DISCUSSION

The Apparent Thermodynamic Ideality of Electrolyte Solutions in Sulphuric Acid.

The apparent thermodynamic ideality of solutions of electrolytes in sulphuric acid observed by Hammett (7, 8) lead Gillespie (5) to assume ideality and postulate that the dielectric constant of sulphuric acid should be greater than that of any solvent yet measured. An alternative interpretation of the observed behaviour is that circumstances combine to give a non-ideal solution whose departure from ideality is constant irrespective of the concentration of the electrolyte. The measurements described lead to a dielectric constant ($\epsilon \sim 110$) for sulphuric acid which is not higher than that of other associated solvents (p. 3), and the alternative interpretation would appear more worthy of consideration.

A convenient description of the departure from ideality is by the coefficient g (the "osmotic coefficient") which in the present circumstances is effectively the ratio of the actual freezing point depression to the ideal value for the same solute concentration. This coefficient may be introduced into Gillespie's freezing point equation (Reference (5), Eqn. 4):-

$$\frac{\Delta\theta}{\Delta m_2} = g\,\nu_2\,k_f\left[1 - 0{\cdot}0035\bar{\theta} + \left\{\frac{(2s_2 - \nu_2)\nu_2\bar{m}_2 + (\nu_3 s_2 + \nu_2 s_3 - \nu_2\nu_3)m_3}{\nu_2 m_2}\right\}\right]$$

where $\bar{\theta}$ is the mean freezing point depression and $\bar{m}_2$ is the mean molality of solute A over finite intervals $\Delta\theta$ and Δm_2, $k_f = \frac{RT_o^2}{m_1 \Delta H_o^f}$ is the cryoscopic constant and

for solute A $\quad A + s_2H_2SO_4 = pP + qQ + rR + \ldots\ldots$

$$p + q + r + \ldots = \nu_2$$

for solute B (water) $\quad B + s_3H_2SO_4 = xX + yY + zZ + \ldots\ldots$

$$x + y + z + \ldots = \nu_3$$

Taking $k_f = 6.12$ deg. g.-mol.$^{-1}$ kg. for the cryoscopic constant, calculated from the latent heat of fusion (ΔH_o^f) found by Rubin (61), the coefficient g has been calculated from several of Gillespie's experiments picked at random and is shown in Table 7. It is seen that the values are all less than unity (the value for ideal solutions), but change only very slightly over five-fold change in composition.

The departure from ideality of aqueous electrolyte solutions has been interpreted by the Debye-Hückel theory which takes into account the interionic forces and the ionic separation. This theory leads (62) to equations for the mean activity coefficient ($\gamma_\pm$) and the osmotic coefficient:-

$$-\log \gamma_\pm = \frac{A z_+ z_- \sqrt{I}}{(\epsilon T)^{3/2}\left[1 + \frac{Ba}{(\epsilon T)^{1/2}}\sqrt{I}\right]}$$

$$1 - g = \frac{C z_+ z_- \sqrt{I}}{(\epsilon T)^{3/2}} \cdot \sigma\left(\frac{Ba}{(\epsilon T)^{1/2}}\sqrt{I}\right)$$

Table 7. Osmotic Coefficients from Freezing Point Data.

Solute	Solvent	Δm_2	$\Delta\theta$	g
Me_2CO	molality H_2O	0.0169	0.200	0.970
$s_2=1$ $\nu_2=2$	$(m_3)=0.045$	0.0282	0.337	0.975
$s_3=1$ $\nu_3=2$	fp. 10.016°C	0.0476	0.565	0.970
		0.0671	0.799	0.975
		0.0864	1.028	0.975
		0.1158	1.383	0.980
MeCOOH	molality H_2O	0.0332	0.397	0.979
$s_2=1$ $\nu_2=2$	$(m_3)=0.050$	0.0462	0.553	0.978
$s_3=1$ $\nu_3=2$	fp. 9.977°C	0.0609	0.721	0.968
		0.1166	1.389	0.974
		0.1533	1.828	0.975
K_2SO_4	molality H_2O	0.0499	1.198	0.980
$s_2=1$ $\nu_2=4$	$(m_3)=0.045$	0.0590	1.429	0.990
$s_3=1$ $\nu_3=2$	fp. 10.022°C	0.0700	1.701	0.991
		0.0803	1.960	0.997

Table 7. (continued)

Solute	Solvent	Δm_2	$\Delta\theta$	g
$(NH_4)_2SO_4$	molality H_2O	0.0141	0.331	0.956
$s_2=1$ $\nu_2=4$	$(m_3)=0.058$	0.0285	0.669	0.958
$s_3=1$ $\nu_3=2$	fp. 9.837°C	0.0423	1.000	0.965
		0.0739	1.762	0.974
		0.0845	2.023	0.978
		0.1083	2.598	0.980
H_2O	molality H_2O	0.0863	0.935	0.887
$s_2=s_3=1$	$(m_3)=0.065$	0.1075	1.167	0.888
$\nu_2=\nu_3=2$	fp. 9.821°C	0.1283	1.396	0.890
		0.1496	1.642	0.900
		0.1712	1.876	0.898
		0.1909	2.099	0.903

where A = 1.82 x 10^6, B = 5.01 x 10^{-7}, and C = 1.40 x 10^6, are composed of universal constants, I = ionic strength, ϵ = dielectric constant, T = absolute temperature, a = mean distance of closest approach of two ions, and $\sigma\left(\frac{Ba}{(\epsilon T)^{1/2}}\sqrt{I}\right) = \sigma(x)$ is the function

$$\sigma(x) = \frac{3}{x^3}\left\{1 + x - \frac{1}{1+x} - 2\ln(1+x)\right\}$$

For a given solvent and temperature values of $\gamma_\pm$ and g can be obtained which may be adjusted by the parameter a. Taking ϵ = 110 and T = 293°K and for molalities between 0.04 and 0.2 (in which range lie most of Gillespie's solute concentrations) g and $\gamma_\pm$ for a 1:1 electrolyte have been calculated (Table 8), for various values of a. From these results it is apparent that a reasonable agreement with experiment is obtainable using values of a ($\sim$ 7Å) which are comparable to the molecular diameter of the solute.

Table 8. Calculated Activity Coefficients and Osmotic Coefficients for a 1:1 Electrolyte in H_2SO_4 at 20°C.

m	$\sqrt{I}$	a	$-\log \gamma_\pm$	$\gamma_\pm$	g
0.04	0.200	5.38	0.0483	0.895	0.968
		6.10	0.0470	0.897	0.969
		7.17	0.0449	0.902	0.971
		10.75	0.0393	0.916	0.976
0.10	0.316	5.38	0.0672	0.857	0.957
		6.10	0.0646	0.862	0.960
		7.17	0.0610	0.869	0.964
		10.75	0.0509	0.889	0.975
0.20	0.447	5.38	0.0843	0.824	0.952
		6.10	0.0797	0.834	0.956
		7.17	0.0741	0.843	0.960
		10.75	0.0629	0.865	0.972

Relation to Sulphonation Kinetics

The kinetics of sulphonation in fuming sulphuric acid have the characteristic that the velocity rises steeply and continuously with increasing sulphur trioxide concentration. This behaviour appears to be accounted for if the sulphonating agent is the ion SO_3^+H, whose concentration is determined by the free sulphur trioxide concentration and the hydrogen-ion activity of the medium, and is a steeply rising function of oleum strength.

The concentration of SO_3^+H ions may be deduced formally from equilibrium (XXXVII)

$$H_2S_2O_7 + H^+ \overset{K_1}{\rightleftharpoons} HSO_3^+ + H_2SO_4 \qquad \text{(XXXVII)}$$

the equilibrium constant being given by

$$K_1 = \frac{\{HSO_3^+\}\ \{H_2SO_4\}}{\{H_2S_2O_7\}\ \{H^+\}} \qquad \text{(XXXVIII)}$$

where the brackets refer to the activities related to the (hypothetical) standard state of an infinitely dilute aqueous solution. Equation (XXXVIII) may be transformed by inserting the definition of the acidity function (6),

$$H_0 = -\log \frac{f_B}{f_{HB^+}} \{H^+\} \qquad \text{(XXXIX)}$$

the f's being activity coefficients of the acid-base pair,

HB^+-B, relative to the standard state in water. In addition $\{H_2S_2O_7\}$ and $\{H_2SO_4\}$ may be evaluated in terms of equilibrium (XL)

$$H_2SO_4 + SO_3 \overset{K_2}{\rightleftharpoons} H_2S_2O_7$$
$$K_2 = \frac{\{H_2S_2O_7\}}{\{H_2SO_4\}\{SO_3\}} \qquad \text{(XL)}$$

(XXXVIII), (XXXIX), and (XL) thus give

$$\log \{SO_3^+H\} = \log (K_1K_2) + \log \{SO_3\} - H_o + \log \frac{f_{HB^+}}{f_B}$$

where K_1 and K_2 are the thermodynamic dissociation constants. Transfering to a standard state in sulphuric acid and collecting constant terms we have

$$\log [SO_3^+H] = A + \log p_{SO_3} - H_o + \log \frac{\gamma_{HB^+}}{\gamma_B \cdot \gamma_{SO_3^+H}} \qquad \text{(XLI)}$$

where A is a term which is constant at constant temperature, the γ's are activity coefficients relative to an infinitely dilute solution in pure H_2SO_4, and p_{SO_3} is the equilibrium vapour pressure of the oleum medium.

Experimentally, sulphonation is a first order reaction, therefore

$$-d[ArH]/dt = k_1 [ArH] \qquad \text{(XLII)}$$

The mechanism to be tested is,

$$ArH + SO_3^+H = ArSO_3H + H^+$$

hence (63) (XLIII)

$$-d[ArH]/dt = k [ArH] [SO_3^+H] \frac{\gamma_{ArH} \cdot \gamma_{SO_3^+H}}{\gamma_\pm}$$

where $\gamma^{\ddagger}$ is the activity coefficient of the activated complex. Comparing (XLII) and (XLIII),

$$k_1 = k[SO_3^+H]\ \frac{\gamma_{A\cdot H}\,\gamma_{SO_3^+H}}{\gamma^{\ddagger}} \qquad \text{(XLIV)}$$

and inserting (XLIV) in (XLI) yields

$$\log k_1 = \log k + A + \log p_{SO_3} - H_o + \log \frac{\gamma_{A\cdot H}\,\gamma_{HB^+}}{\gamma^{\ddagger}\,\gamma_B} \qquad \text{(XLV)}$$

Equation (XLV) must, therefore, account for the dependance of the experimental rate coefficient (k_1) upon the oleum strength (expressed as log p_{SO_3} and H_o) if mechanism (XLIII) is correct.

The substances chosen for the sulphonation experiments are of two classes, (a) quaternary ammonium compounds, that is derivatives of $Ph\overset{+}{N}Me_3$, and (b) aromatic nitro-compounds. The latter are partially ionised in the oleum media;

$$ArNO_2 + H_2S_2O_7 = ArNO_2^+H + HS_2O_7^-$$

but only the non-ionised molecules, $ArNO_2$, undergo sulphonation, thus the velocity coefficient is referred to these molecules only. It is also significant that the H_o function in oleum has been determined from the degree of ionisation of similar nitro-compounds (3,64); therefore B and HB^+ in equations (XXXIX), (XLI) and (XLV) refer to $ArNO_2$ and $ArNO_2^+H$ respectively.

For the case of sulphonation of the quaternary ammonium system, the activity coefficient quotient in

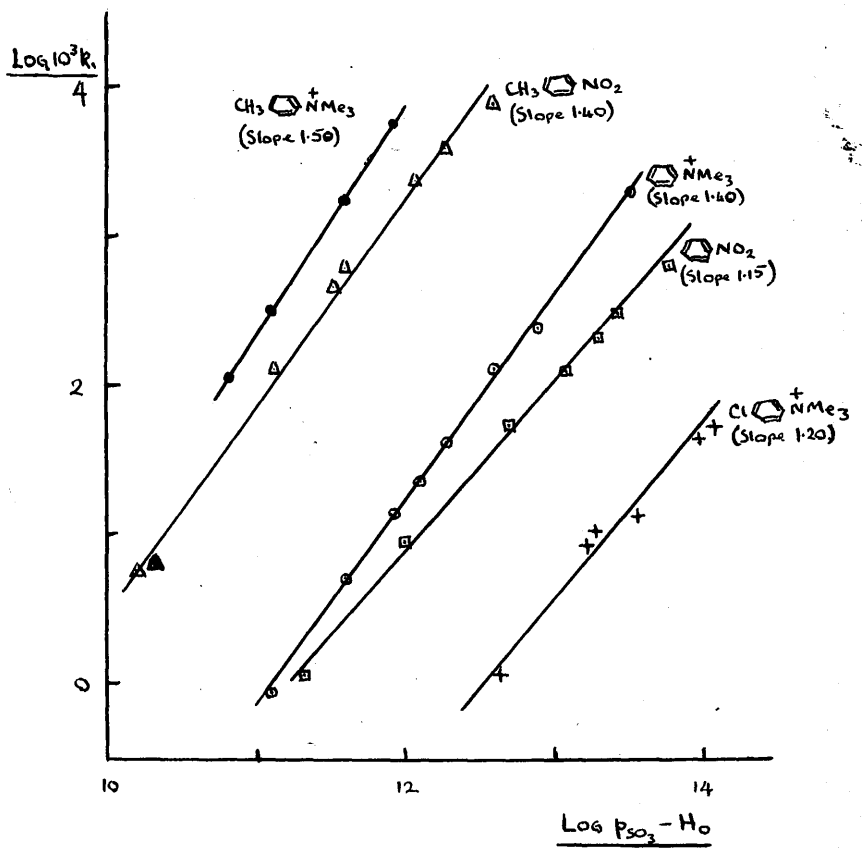


Fig. 18. Variation of Velocity of Sulphonation with Theoretical Concentration of SO_3H^+. (25°C).

Equation (XLV) becomes $\frac{\gamma_{A\cdot NMe_3}\,\gamma_{HB^+}}{\gamma^{\ddagger}_{(2+)}\;\gamma_B}$, the transition state being a divalent ion. The corresponding expression for the sulphonation of a nitro-compound is $\frac{\gamma_{A\cdot NO_2}\,\gamma_{HB^+}}{\gamma^{\ddagger}_{(+)}\;\gamma_B}$, which is symmetrical with respect to charge and probably close to unity in a solvent of high dielectric constant, particularly since B, in general, stands for aromatic nitro-compound.

Equation (XLV) is tested by plotting log k_1 (3,64) against (log p_{SO_3} - H_0) (Fig. 18). The actual relation is close to linearity with slopes between 1.15 and 1.50. The slope will only be unity if the activity coefficient term is independant of oleum concentration. It is not necessary that exact linearity should be maintained where departures from unit slope occur, linearity would only persist if the activity coefficient term is a linear function of (log p_{SO_3} - H_0).

The correlation shown by the result in Fig. 18 appears to be satisfactory evidence for the identification of the sulphonating agent with SO_3^+H.

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